ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

DEVELOPMENT OF SILVER NITRATE LOADED POLYACRYLONITRILE COMPOSITE NANOFIBERS

M.Sc. THESIS

Nesrin DEMİRSOY

Department of Polymer Science and Technology

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Anabilim Dalı : Herhangi Mühendislik, Bilim
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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

GÜMÜŞ NİTRAT İÇEREN POLİAKRİLONİTRİL KOMPOZİT NANOLİFLERİN GELİŞTİRİLMESİ

YÜKSEK LİSANS TEZİ

Nesrin DEMİRSOY
(515111042)

Polimer Bilim ve Teknolojisi Anabilim Dalı

Polimer Bilim ve Teknolojisi Programı

Tez Danışmanı: Prof. Dr. Hacer Ayşen ÖNEN
Anabilim Dalı : Herhangi Mühendislik, Bilim
Programı : Herhangi Program

OCAK 2015

Nesrin DEMİRSOY, a **M.Sc**. student of ITU **Graduate School of Science Engineering and Technology** student ID 515111042, successfully defended the **thesis**entitled "**DEVELOPMENT OF SILVER NITRATE LOADED POLYACRYLONITRILE COMPOSITE NANOFIBERS**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. Hacer Ayşen ÖNEN** İstanbul Technical University	.....
Jury Members :	**Prof. Dr. Fatoş Yüksel Güvenilir** İstanbul Technical University	.....
	Doç.Dr. İsmail Usta Marmara University	.....

Date of Submission : 15 December 2014
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To my precious family and dearest friends,

FOREWORD

This study has been carried out with the collaboration of the laboratories of POLMAG (Polymeric Materials Research Group) and Textile Engineering Department. I would like to thank to TUBITAK for supporting this study with project (112M877).

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Nesrin DEMİRSOY
(Chemical Engineer)

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ABBREVIATIONS

PAN	**:** Polyacrylonitrile
PVP	**:** Poly(N-vinylpyrrolidone)
DMF	**:** N,N-Dimethylformamide
UV-Vis.	**:** UV-Visible spectroscopy
SEM	**:** Scanning electron microscope
XRD	**:** X-ray differaction
DSC	**:** Differential scanning microscopy
SNp	**:** Silver nano particles
CNF	**:** Carbon nanofiber

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DEVELOPMENT OF SILVER NITRATE LOADED POLYACRYLONITRILE COMPOSITE NANOFIBERS

SUMMARY

Nowadays polymer composite nanofiber materials including silver nano particles have been drawn attention due to their attractive properties which are used in several areas. Silver nitrate ($AgNO_3$) loaded polymer composite nanofibers have been used in wound-healing application, filtering media, chemical and biological protective materials, industrial dust collection systems, air filters or water filters, photonic and electric sensors, artificial tissues, protective textiles etc..

Polyacrylonitrile (PAN) is one of the important engineering material that is used to produce synthetic nanofibers. PAN/Ag composite polymers provide opportunity to obtain functionally fibers due to their gained optical, mechanical, electrical, antibacterial properties. Also providing high specific surface area and high interpenetrating capacity, high electrical conductivity.

Although various properties was obtained from silver nanoparticles embedded polymer composite, dispersion of the silver ion has great importance in the PAN/Ag nanofibers. The properties of these nano composites are related with the size, amount and dispersion quality of the silver nitrate nano particles that embedded into polyacrylonitrile matrix. There are different methods for obtaining a polymer composite matrix. The mechanical mixing of polymer solution and silver nano particles ($AgNO_3$) is one of the easiest methods. Although its simplicity, this method has a major disadvantage that agglomeration of the silver nano particles. Also the homogeneous dispersion of the silver nano particles into the polymer matrix is quite difficult because of the high viscosity of the polymer solution. In chemical reduction method, the reduction of the silver salt could be done in the presence of a suitable stabilizer that required to obtain stable, monodispersed nanoparticles. Poly(N-vinylpyrrolidone) (PVP) is the one of the best stabilizer that used in this area.

Owing to these disadvantages some recent methods that are based on in situ reduction of metal ions and in situ polymerization of monomers have drawn interest. In these methods, silver ions have been provided from metal salt that have been reduced into Ag^0 in the polymeric matrix.

Obtaining of the silver metallic nano particles could be done by different reduction methods such as chemical reduction using sodium borohydrate, heat treatment, reflux method, UV radiation, Xenon arc reduction etc. Electrospinnig is the most used technique among the researchers for the production of polymer fibers containing metal nano particles.

In this thesis the effect of the loading different amounts of the silver nitrate into polymer composites, different dispersion methods, different ratio of PVP loading, the effect of the reduction methods were investigated on the mechanical, electrical properties and antibacterial efficiency of the composite nanofibers.

GÜMÜŞ NİTRAT İÇEREN POLİAKRİLONİTRİL KOMPOZİT NANOLİFLERİN GELİŞTİRİLMESİ

ÖZET

Son yıllarda gümüş nitrat ihtiva eden ve pek çok alanda kullanımı olan nanolifler oldukça ilgi çekmektedir. Gümüş nitrat içeren polimer kompozit nanolifler yara iyileştirme tedavisinde filtrelerde membran olarak, kimyasal ve biyolojik koruyucu malzemelerde, endüstriyel toz toplama sistemlerinde, hava ve su filtrelerinde, ışık ve elektrik sensörü olarak, yapay dokularda ve koruyucu tekstil ürünlerinde kullanılmaktadır.

Poliakrilonitril sentetik nanolif üretiminde kullanılan önemli mühendislik polimerlerinden biridir. PAN/Ag kompozit polimerleri optik, mekanik, elektriksel, antibakteriyel özellikler sağlaması sebebiyle fonksiyonel sentetik nanoliflerin elde edilmesine olanak sağlamaktadır. Ayrıca yüksek yüzey alan, yüksek nüfuz etme kapasitesi ve yüksek elektriksel iletkenlik de sağlamaktadırlar.

Gümüş nanopartikül içeren polimer kompozitler değişik pek çok özellik sağlamasına rağmen, PAN/Ag nanoliflerindeki gümüş iyonlarının dispers edilmesi büyük önem teşkil etmektedir. Polimer matriksin içinde yer alan gümüş iyonlarının miktarı, dağılımı ve boyutu nanoliflerin istenilen özelliklerine oldukça etki etmektedir.

Polimer kompozit malzemelerin eldesi için pek çok yöntem olmasına rağmen polimer solüsyonu ile gümüş nitrat taneciklerinin mekanik karıştırılması en kolay ve bilindik yöntemdir. Uygulamada kolaylık sağlamasına rağmen gümüş nano partiküllerin agglomera olması sebebiyle bu yöntem dezavantajlıdır. Aynı zamanda polimer solüsyonun yüksek viskozitede olması, gümüş nanopartiküllerin dağılımını azaltmakta ve agglomerasyon riskini artırmaktadır.

Gümüş nano partiküllerin homojen dağılımını sağlamak ve istenilen sabit, mono dispers nanopartikül dağılımını elde edebilmek amacıyla kimyasal indirgeme yöntemlerinde stabilizatör kullanımı da yapılabilmektedir. Poly(N-vinylpyrrolidone) (PVP) bu amaçla kullanılan bilinen en iyi stabilizatörlerdendir.

Agglomerasyon gibi olumsuz özelliklerin etkisini azaltmak veya ortadan kaldırabilmek amacıyla metal iyonlarının matriks içinde indirgenmesi son yıllarda dikkat çeken çalışma yöntemlerinden biridir. Bu yöntemle metal tuzlarından elde edilen gümüş iyonları Ag^0'a polimer matriksi içinde indirgenir.

Gümüş iyonlarından gümüş nano partiküllerin elde edilmesi birçok farklı indirgeme yöntemiyle gerçekleştirilebilir. Kimyasal indirgeme metodlarından sodium

borohidratla, refluxla, UV ışımasıyla ve Xenon Arc ile indirgeme işlemi yapılabilmektedir.

Bu tez çalışmasında kompozit nanoliflere eklenen farklı oranlarda gümüş nitrat, farklı oranlarda PVP ve uygulanan farklı dispersiyon yöntemleri ile değişik indirgeme yöntemlerinin nanoliflerin mekanik, elektriksel ve antibakteriyal özellikleri üzerindeki etkileri incelenmiştir.

Çalışmanın ilk aşamasında farklı indirgeme yöntemlerinin parametreler üzerindeki etkileri incelenmiştir. Bu sebeple ilk etapta %10 gümüş nitrat içeren nanolifler üretilmiştir. Üretilen nanolifler üzeride beş farklı indirgeme yöntemi kullanılmıştır. Bunlar; hidrazin hidroksitle indirgeme, refluks yöntemi, Xenon Arc lambası ile solüsyonda indirgeme, xenon arc lambası ile nanolif üzerinde indirgeme ve UV lambası ile indirgeme yöntemleridir.

Hidrazin hidroksitle indirgeme yönteminde hidrazin hidroksitin belli oranda sulu çözeltisi hazırlanmıştır. Elektroeğirme yöntemi ile üretilmiş nanolifler, bu sulu çözelti içinde belli bir süre bekletilerek indirgenmiştir.

Refluks yöntemi ile gümüş nitrat içeren PAN/$AgNO_3$ solüsyonu refluks düzeneği kurularak indirgenmiştir.

UV lambası ile indirgemede ışıma kutusu yapılmış ve içine nanolifler yerleştirilerek belirli sürelerde indirgenme sağlanmıştır.

Xenon arc lambası kullanılarak yapılan indirgemede iki yol izlenmiştir: PAN/$AgNO_3$ solüsyon olarak indirgenmiş, indirgenmiş nanopartiküller ile elektrospinnig yapılmıştır. Diğer yöntemde ise PAN/$AgNO_3$ solüsyonu üretilip elektrospinning yapılır. Elde edilen nanolif Xenon lambasında indirgenir. Xenon arc lambası yüksek yoğunluğa sahip iyonlaşmış ksenon gazına elektriksel potansiyel uygulayarak ışık üreten bir gaz deşarj lambasıdır. Ve gün ışığına benzeyen parlak beyaz bir renk üretir. Fakat görünür bölgede ışıma verme konusunda etkin değildir.

Çalışmanın diğer aşamasında, gümüş nitrat dispersiyonunda stabilizatör etkisini incelenmiştir. Bu amaçla PVP kullanılmıştır. PVP bu amaçla kullanılan stabilizatörler arasında en etkin olanıdır. PVP'nin etkilerini incelemek için PAN/$AgNO_3$ solüsyonuna belirli oranlarda PVP eklenmiş ve elektrospinning yapılmıştır. Aynı zamanda PVP içeren nanoliflerin farklı yöntemlerle (hidrazin ve xenon arc solüsyon yöntemleri) indirgenmesiyle elde edilen parametreler de incelenmiştir.

Tezin diğer bir aşamasında karıştırma, dispersiyon, yöntemlerinin etkileri incelenmiştir. Bu nedenle iki farklı karıştırma yönteminin karşılaştırılması yapılmıştır. Magnetik karıştırma ve ultasonik karıştırma yöntemleri karşılaştırılmıştır. En etkili karıştırma yöntemi tespit edilmiş ve bu yöntemin incelenen özellikler üzerindeki etkileri tespit edilmiştir.

Tezin en önemli çalışmalarından biri de elektriksel iletkenlik, mukavemet, antimikrobiyal özelliği sağlamada en etkin gümüş nitrat oranının belirlenmesidir. Bu sebeple farklı oranlarda (%1, %3 ve %10) gümüş nitrat içeren PAN/$AgNO_3$ çözeltileri hazırlanmış, elektroeğirme yöntemi ile nanolif haline getirilmiş ve çeşitli yöntemlerle

indirgenmiştir. Aynı şeklide solüsyon halindeki PAN/$AgNO_3$ karışımları çeşitli yöntemlerle indirgendikten sonra elektroeğirme ile nanolif haline getirilerek istenen özelliklere olan etkileri incelenmiştir.

Nanolif üretiminde pekçok yöntem kullanılmakla birlikte, elektroeğirme yöntemi, pürüzsüz, düzgün ve güvenilir nanolif elde etmede en yaygın kullanılan yöntemlerden biridir. Bu yöntemle morfolojisi kontrol edilebilen nanolifleri üretebilmek mümkündür.

Elektroeğirme yöntemi, yüksek elektrik alan ile yüklenmiş polimer solüsyonlarından nanolif üretimine dayanan bir yöntem olup nanolif üretiminin elektriksel kuvvetlerle kontrol edilebildiği bir yöntemdir.

Bu çalışmada üretilen nanoliflerin karakterizasyonu sırasında pek çok cihaz ve yöntem kullanılmıştır. Elektriksel iletkenlik için iletkenlik ölçer cihazı, mukavemet değerlerinin ölçümünde mukavemet cihazı, morfolojik özelliklerin incelenmesinde SEM, SEM-EDS ve XRD cihazı, nanoliflerin termal özelliklerin incelenmesinde DSC cihazı, indirgenme etkisini ve gümüş nitrat katkısının sağladığı etkileri görebilmek amacıyla UV-Visible cihazı kullanılmıştır. Ayrıca antimikrobiyal etkinlik testleri de *Staphylococcus aureus* bakterisine karşı yapılmıştır.

Yapılan çalışmalar sonucunda elektriksel iletkenlikte, mekanik özelliklerde, antimikrobiyal etkinlikte, nanolif çapında, termal özelliklerde en etkin indirgenme yöntemi, gümüş nitratların dispersiyonunda en etkin karıştırma yöntemi, gümüş nitratın dispersiyonunda katkı sağlamak amacıyla kullanılması gereken etkin PVP oranı belirlenmiştir. Aynı zamanda bahsi geçen özelliklerin en iyi netice verdiği gümüş nitrat oranı tespit edilmiştir.

Buna göre; elektriksel iletkenlikte en uygun gümüş nitrat katkısının %3 oranında olduğu görülmüştür. En etkin mukavemet değerlerinin %1 katkılı gümüş nitrattan elde edildiği sonucuna ulaşılmıştır. PAN solüsyonuna gümüş nanopartikül eklenmesinin indirgeme olmadan bile mukavemeti arttırdığı görülmüştür. Ayrıca gümüş nitrat katkısının nanolif çaplarını artırdığı tespit edilmiştir.

İndirgeme yöntemlerinden xenon arc solüsyon yönteminin en kalın nanolif çapına neden olduğu görülmüştür. Bu duruma bu yöntemle indirgemenin solüsyon viskozitesini artırmasının neden olduğu düşünülmüştür.

İndirgeme yöntemlerinden hidrazin hidroksitle ve xenon arc solüsyon yönteminin en etkili sonuçları verdiği görülmüştür. Fakat sanayide uygulama kolaylığı sağlama açısından, hidrazin hidroksit yönteminin daha pratik sonuçlar verebileceği düşünülmüştür. Hidrazinle indirgenmiş nanoliflerin daha dayanımlı nanolifleri elde etmede olumlu etkileri görülmüştür.

Gümüş nitratların dispersiyonunu kolaylaştırmak amacıyla stabilizatör olarak kullanılan PVP için 1:1 oranının en etkili sonuç verdiği görülmüştür. Ancak PVP'nin uygun oranlarda kullanılmasının dispersiyon açısından olumlu sonuçlar verdiği sonucuna ulaşılmıştır.

Antimikrobiyal etkinlik açısından incelenen %10 gümüş nitrat içeren nanoliflerde her üç indirgeme yönteminin (hidrazin hidroksit, xenon arc solüsyon, xenon arc nanoweb) de etkili sonuç verdiği görülmüştür. Üç farklı yöntemle indirgenen %10 gümüş nitrat içeren nanoliflerde %99 oranında antimikrobiyal etkinlik sağlanmıştır. Antimikrobiyal etkinlik sağlamada minimum %3 oranında gümüş nitrat kullanımının yeterli olabileceği sonucuna varılmıştır.

1. INTRODUCTION

Polyacrylonitrile/silver nitrate composite nanofiber materials have gained very important place in some industrial usages and applications. The nano-effect that comprised of incorporation of silver nitrate into the polymer matrix solution can provide various desirable properties such as strength, high surface energy and reactivity and electrical conductivity to the electrospun nanofibers. Including of silver metal nanoparticles into the nanofibers offers dual functionality so that these nanofibers have promising applications in many fields. These composite materials can be used as catalyst, electric sensors, filters. Also, PAN/Ag composite nanofibers are used in protective textiles, medical applications, biomedical science. Polyacrylonitrile (PAN), has been widely used in producing nanofibers and it is a wellknown polymer due to having good stability and mechanical properties.

In recent years, in situ synthesis of metal nanoparticles have been drawn attention among the researchers. In this method, the reduction of the dispersed metal (silver) ions is done in polymer matrices. There are different reduction methods for obtaining silver nanoparticles such as reducing with heat, UV-light, sodium borohydride etc. It is aimed that the negative effect of agglomeration of silver metal nanoparticles to be decreased by these in situ reduction methods.

In situ preperation of nanofiber films from well dispersed PAN/$AgNO_3$ solution was obtained by electrospinning technique. In the electrospinning system, a high-voltage power supply was used to generate an electric field. A positive voltage was applied to needle tip and the negative voltage was connected to the collector that covered with aluminum foil. A nonwoven nano-fiber mat was covered on the aluminum foil for collecting the produced nano-fibers.

Decrease of the agglomeration can be achieved by using stabilizers with the polymer solution. Stabilizers are used to protect silver nano particles from the agglomeration. The stabilizers provide reaction between functional groups of stabilizer and silver nano particles so that they decrease the possibility of coalescence of silver nano particles. There are several stabilizers that are used in nano particles synthesis such as gelatin, D-sorbitol, poly(N-vinylpyrrolidone) (PVP), polyvinyl alcohol (PVA) and poly(methylvinylether) (PMVE). PVP is known as the best stabilizer for the silver nano particles due to being an excellent dispersant among the all other stabilizers.

In this study, the effect of different reduction methods, the effect of different amount of silver nitrate loading and different amount of stabilizer (Poly(N-vinylpyrrolidone)-PVP) on mechanical, electrical, antibacterial properties of polyacrylonitrile composite nanofibers were investigated in detail to determine the most suitable reduction method and the effect of PVP loading on the structure and the properties of the final product. PAN/$AgNO_3$ composite nanofibers were produced by electrospinnig method. Characterization of the nanofibers were done by differential scanning calorimetry,

tensile tester, conductivity meter, UV- visible spectroscopy etc. The antibacterial efficiency test results was also obtained against to *Staphylococcus aureus* bacteria.

2. THEORETICAL PART

2.1 Polyacrylonitrile

PAN is an atactic, linear polymer containing highly polar nitrile pendant groups. Because of its highly polar nature, pure PAN has a glass transition temperature of approximately 120 °C and tends to decompose before it melts. Therefore, PAN precursor fibers must be produced by either wet- or dry-spinning processes using highly polar solvents. Actually, PAN homopolymer is rarely, if ever, used as a carbon fiber precursor. Commercial PAN precursor fibers normally contain from 6 to 9% of other monomers, such as itaconic acid, acrylic acid, methacrylic acid, methyl acrylate, vinyl bromide, etc. These additions lower the glass transition temperature and affect the reactivity of the polymer structure. Both of these changes can dramatically influence subsequent process steps [1].

Polyacrylonitrile (PAN) and copolymers of PAN have been widely studied for almost a century for commercial/technological exploitations. PAN may be crosslinked, but also may exist without crosslinking. Crosslinking of PAN will impart some of its important physical properties, such as insolubility and resistance to swelling in common organic solvents. Recently, considerable efforts have The chemistry of PAN is of particular interest because of its use as a precursor in the formation of CNFs for different applications, including porous structured CNFs of high surface area for electronics and energy storage applications as well as graphite reinforcement filaments for organic materials in high strength and high stiffness composites [2].

2.2 Polyacrylonitrile as a fiber

Even though acrylonitrile (AN) was known as far back as 1893, but PAN, because of difficulties in dissolving it for spinning, no progress was made in converting into a usable fiber until 1925. Acrylonitrile monomer was also useful as a copolymer with

styrene, especially in a terpolymer with styrene and butadiene, known as ABS rubber. The homopolymer of PAN was developed for manufacturing of fibers in 1940, after a suitable solvent was discovered by DuPont. PAN is soluble in polar solvents like DMF, DMSO, DMAc, dimethylsulfone, tetramethylsulfide and aqueous solutions of ethylene carbonate, as well as some mineral salts. PAN forms saturated solution with 25% dissolved in DMF at 50 ◦C, which is high solubility compared to other solvents [3].

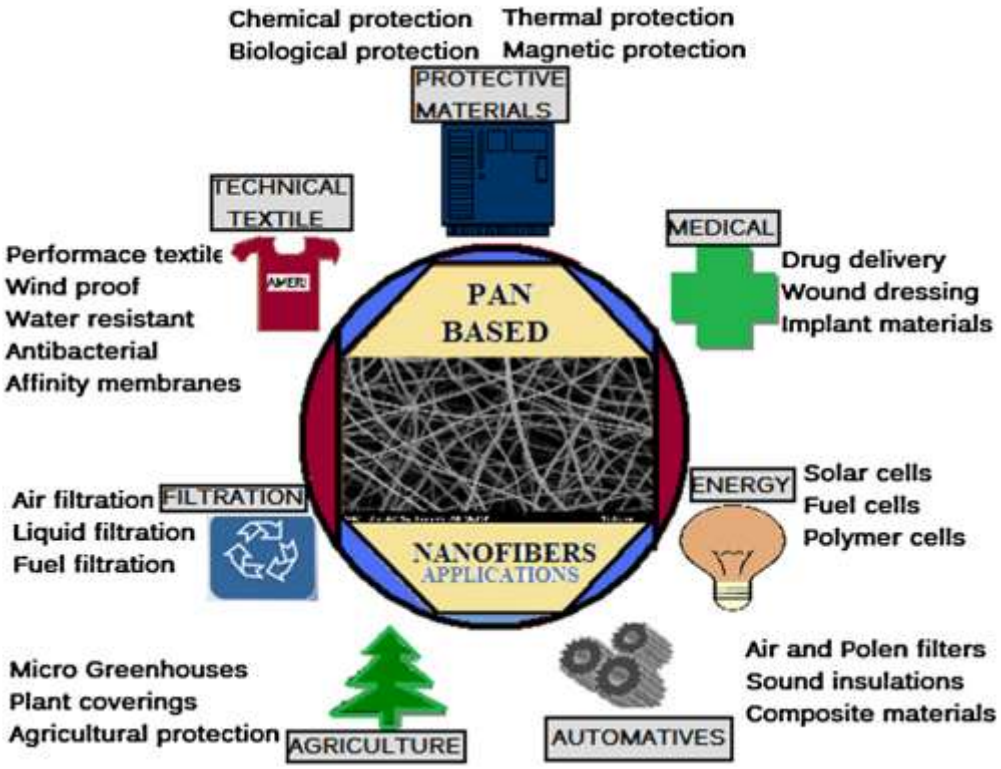

Figure 2.1 : Usage areas of PAN nanofibers [2].

PAN and its copolymers are predominantly white powders up to 250 ◦C, at which point they become darker due to degradation. Having a relatively high T_g, these polymers have low thermal plasticity and cannot be used as a plastic material. The high crystalline melting point (317 °C) of PAN, its limited solubility in certain solvents coupled with superior mechanical properties of its fibers is due to intermolecular forces between the polymer chains. Appreciable electrostatic forces occur between the dipoles of adjacent – C = N groups and this intramolecular interaction restricts the bond rotation, leading to a stiffer chain [4]. The properties of CNFs are strongly dependent on the microstructure of the stabilized PAN fiber [5–6].

There are a number of methods to produce nanofibers, e.g., vapor growth [7], arc discharge [8], laser ablation and chemical vapor deposition [9]. However, these are very expensive processes due to low product yield and the expensive equipment required. On the other hand, the electrospinning method, invented in 1934, can generate fibers with diameters from 10 nm to 10 micro meter [10] from a polymer solution under the application of an electrostatic force. The applied electric field and solution conductivity are important parameters that influence the fiber diameter during the spinning, in addition to parameters such as the jet length, solution viscosity, surrounding gas, flow rate, and the geometry of the collector are important [11-12].

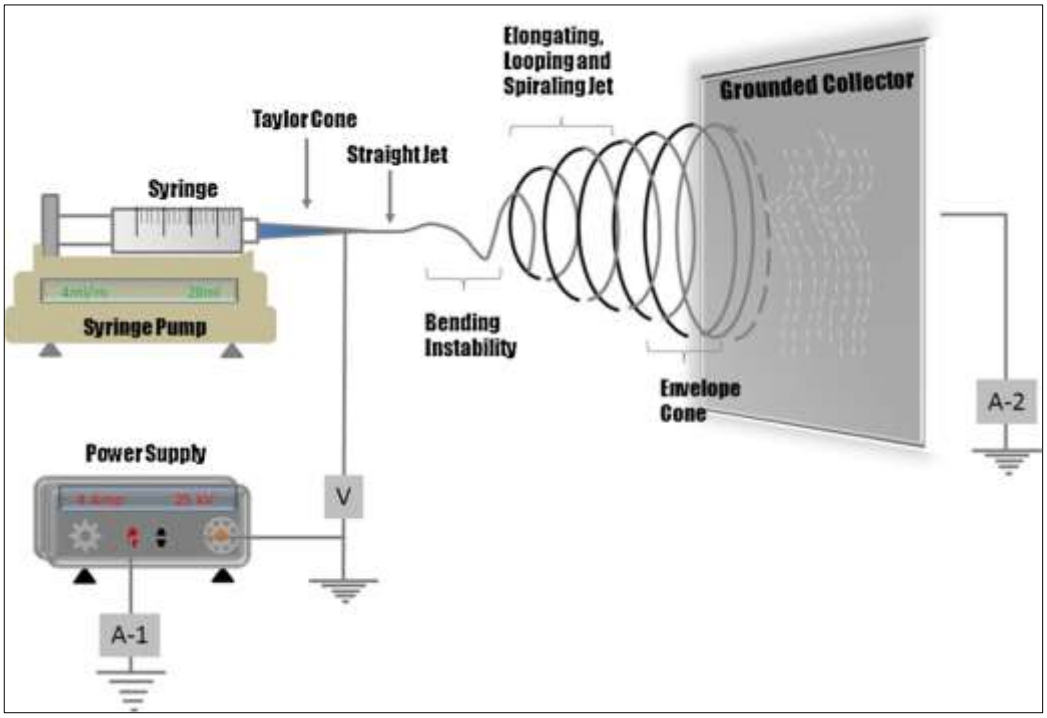

Figure 2.2 : Electrospinning system [2].

2.3 Electrospinning

Nanofibers are a unique class of nanomaterials with many interesting properties owing to their nanoscale diameters and large aspect ratio. They possess excellent mechanical properties and their surface can be readily modified due to their high surface area to volume ratio [13]. Nanofibers can be produced with different techniques such as drawing [14], template synthesis [15], phase separation [16], selfassembly and

electrospinning [17]. Among these, electrospinning is rapidly emerging as a simple and reliable technique for the preparation of smooth nanofibers with controllable morphology from a variety of polymers [18]. Electrospinning involves the application of a high electric field to generate nanofibers from a charged polymer solution ormelt.

Careful control of operating conditions and solution parameters can lead to the production of highly porous structures of smooth, defectfree non-woven nanofibrous membranes [19]. Fiber formation in the electrospinning process is driven by repulsive electrostatic forces. Coulomb interactions in the charged fluid jet result in jet instabilities that dictate the end architecture of the fibers [20]. These instabilities cause the polymer jet to form a Taylor cone at the needle tip. Due to the forces acting on it, the jet eventually exits the needle and thinning occurs. As the jet thins, the solvent evaporates leaving behind polymer fibers which are deposited on a grounded collector. Jet instabilities that result from the rheological behavior of the polymer fluid are crucial in determining fiber formation [21]. Most instabilities cause breakage and prevent the formation of continuous fibers. However, the bending instability is crucial to fiber formation: nanofibers are formed when the charged polymer jet bends in expanding loops and is then collected on a substrate [21].

Electrospinning is a highly versatile technique in that the surface topography, fiber morphology and orientation are largely dictated by solution properties and operating conditions. Since the rheology of the polymer solution is vital to the fiber formation process, solution properties such as polymer molecular weight and concentration directly affect fiber properties. Conductivity of the polymer solution is also known to change properties of the resultant fibers. Fiber properties are also directly affected by operating conditions such as applied voltage, solution flow rate and tip-collector distance. Ambient conditions such as temperature and humidity of the electrospinning chamber can also alter fiber morphology.

2.3.1 Substance parameters of electrospinning

Generally the polymer solution must have a concentration high enough to have a sufficient number of polymer entanglements, yet not so high that the viscosity prevents sufficient polymer flow being induced by the (low pressure) pump and sufficient stretching being induced by the electrical field [22]. The solution must also have a low

enough surface tension, a high enough charge density and be sufficiently viscous to prevent the jet from coalescing into droplets before the solvent has evaporated [23]. It has been recognised that the intrinsic properties of the polymer such as molecular weight [24], molecular weight distribution and architecture (branched, linear, etc.) of the polymer could affect the concentration range that is suitable for electrospinning fibres. For instance, in electrospinning of poly(ethylene oxide) in aqueous solution at low concentration, beaded fibres are often found [24] owing to the low solution viscosity and the relative high surface tension (as well as there being insufficient force to stretch the polymer jet). With increasing viscosity (proportional to the concentration), the beaded fibres disappear and are replaced by smooth cylindrical fibres, and an even higher viscosity results in a larger fibre diameter. Moreover, considerably increasing the conductivity, by addition of salts [24 – 26] or drugs [27] or increasing the polarity of a solvent mixture increases the net charge density and results in a marked increase of Coulombic repulsion.

2.3.2 Process parameters of electrospinning

The structure and morphology of electrospun fibres is also affected by the applied electrical potential and the distance between tip and collector because these parameters directly affect the deposition time, evaporation rate and whipping or instability regions. In general, for a given solution viscosity and polarity, a higher electrical potential ejects more fluid in a jet, resulting in a larger fibre diameter [25] whereas a shorter tip–collector distance tends to produce wetter fibres and thus beaded structures. Evaporation rate affects the fibre formation process because the loss of solvent increases the viscosity (exponentially as the glass transition temperature, *T*g, is approached) during spinning reducing the tendency to form beads via a Rayleigh instability. Aqueous polymer solutions require longer distances to form dry cylindrical fibres than systems that use highly volatile organic solvents [22]. Ambient temperature and humidity are also very important process parameters, owing to their influence on the solvent evaporation process and the resultant fibre morphology. Moreover, electrospinning in a very humid environment is another route to porous fibres [28] where tiny droplets of water precipitate onto the jet and generate phase separation. These droplets then form pores in the solidified fibre after solvent evaporation. The extent of pore formation and the pore size can be tuned by varying the humidity.

Great variation in fibre assemblies and morphologies can be effected through the design and construction of the electrospinning apparatus (or setups) and, obviously, the key to making reproducible fibres and assemblies is to control the spinning environment. In many cases the purpose of modifications to the process is to improve control or tailor the process to suit the needs of specific materials and applications. There are three main categories of modification to the apparatus for electrospinning: the spinneret, manipulation of the electric field (controlling fibre deposition) and the collector. By modifying the spinneret design, different properties can be introduced into the ultrafine fibre. Coaxial (or dual-capillary) spinneret design has been utilised by various researchers either to protect or to exhibit functionalising agents or to electrospin material that cannot otherwise be electrospun perhaps owing to high surface tension or low molecular weight. For commercial activities in the fibre production and utilisation industries, one important consideration is the rate of production of fibre assemblies. Much work has been done on the use of multiple spinnerets [29,30] for fabricating fibres. Another method to obtain a high rate production of fibres is using a needleless spinning setup which ensures constant renewal of the solution surface without the problem of needle clogging or droplet setting and enables spinning over a larger area. During the electrospinning process, the force that stretches the solution into a fine strand is the electrostatic charge applied to it using a high voltage power supply. Since the electrostatic charges are distributed along the electrospinning jet, an external electric field can be used to control the jet. To manipulate the external electric field so as to exert some control on the electrospinning jet, the shape, position and polarity of the charges applied to the auxiliary electrodes (such as electrostatic lenses) have to be considered. Since the profile of the electric field between the tip of the spinneret and the collector has an influence on the electrospinning jet, a number of approaches (each with a different way of controlling the distribution of electric field) have been demonstrated to create aligned or patterned fibres. One very simple method uses a rotating wheel, drum or frame as a collector [31]. Another common technique uses a pair (or an array) of electrodes in parallel. The arrangement and the patterns formed by the fibres, however, are different throughout the fibre mesh and depend on their location in the gap.

Electrospinning has the unique ability to produce ultrafine fibres of different materials in various fibrous assemblies. Owing to their submicrometre size, electrospun fibres

are able to form a highly porous mesh and their large surface area to volume ratio improves performance for many applications.

High porosity, interconnectivity, microscale interstitial space and a large surface area to volume ratio mean that nonwoven electrospun fibre meshes are an excellent material for membrane preparations and uses such as filters [32] and textiles. Electrospun nanofibres can form an effective size exclusion membrane for particulate removal from wastewater. The filtration efficiency of a nanofibre membrane has been studied [33] finding that the nanofibrous membrane was extremely effective for the removal (~100% rejection) of airborne particles with diameters between 1 mm and 5 mm by both physical trapping and adsorption. Layered fabric systems with electrospun zinc oxide composite fibre webs were developed, at various concentrations of zinc oxide, in a range of web area densities. It was found that a very thin layer of electrospun zinc oxide composite fibres significantly increased the UV blocking for both UV-A and UV-B ranges, and exhibited an ultraviolet protection factor of greater than 40, indicating excellent UV protection. Increasing the electrospun web area density of the zinc oxide nanocomposite fibre web also enhanced the UV-protective properties of layered fabric systems. Even though electrospun fibrous membranes can exhibit great advantages over conventional media in environmental applications, such as air and water filtration, there still remain many challenges in their applications as filters and textiles, such as the low mass production rates for high quality ultrafibres and ultrafibre-based composites and the selection of suitable materials and appropriate chemistry to introduce the desired functionality to meet specific needs. None of these challenges are trivial but they are also not insurmountable. New approaches in structure manipulation (such as core-shell nanofibres and bi-/multi-component nanofibres) and modification of nanofibre surfaces (chemical grafting and plasma treatment) have been rapidly demonstrated. These new processes and new chemistries may all be incorporated in the fabrication of better (e.g. higher flux, more efficient and stronger) filtration membranes and texture.

One of the most important applications of traditional (micro-size) fibres, especially engineering fibres, is their use as reinforcements in composites. With these reinforcements, the composite materials can provide superior structural properties such as high modulus and strength to weight ratios, which generally cannot be achieved by other monolithic engineered materials alone. This methodology can also

be applied to electrospun nanofibres for medical applications. Fibrous polymer structures can be applied as the supporting matrix or template, and hence superior structural properties in nanocomposites can be anticipated. A variety of functional components can be directly added to the solution for electrospinning to obtain nanofibres with a diversified range of compositions and well-defined functionalities Meanwhile, electrospun polymer fibres can be used as templates in the preparation of hollow fibres to produce nanofibers.

Electrospun fibres are also being explored for use in many other functional applications, such as micro/nano electronic devices, sensors and catalysis, all of which could have useful biomedical applications. Nanofibres from polymers with piezoelectric effects will make the resultant nanofibrous devices piezoelectric. Electrospun polymer nanofibres could also be used in developing functional sensors, with the high surface area of nanofibres facilitating increased.**2.4 History of Silver**Silver has been used for thousands of years as a precious metal by humans in different applications as jewellery, tools, coins, photographic material or explosives [34]. One of the most significant use of silver is as a disinfectant with hygienic for medical purposes. Since the ancient times, silver vessels were used for the storage of water or wine because it was believed that this metal preserved their conditions. Also Hippocrates described the use of silver powder for its application in wound healing and in the treatment of ulcers. In the 17th and 18th centuries, silver nitrate was used for ulcer treatment and its antimicrobial activity was established in the 19th century. Nevertheless, after the introduction of the antibiotics in 1940 the use of silver salts decreased. Subsequently silver salts and silver compounds have been used in different biomedical fields, especially in burn treatment [35]. The chemical synthesis of silver nanoparticles is a well established research field, although not deliberated, from centuries ago. The first recognized example is the bronze Lycurgus cup from the IVth century AD that possesses colored glass that disperses green light and transmits red light due to its content on an alloy of silver (70%) and gold (30%) nanoparticles [36]. Another curious example is the metallic luster which is a kind of ceramic decoration that consists of the use of silver nanoparticles, among other metals, for producing a beautiful metallic shine and colored iridescence on the surface of the ceramic object. After the ninth century this technology was spread from Iraq to Persia, Egypt, Spain and Italy [37].

The previously described historical examples are the starting point for the development of the silver-based nanomaterials. Nowadays, the most active working fields related to silver nanoparticles are the study and application of their optical and biomedical properties.

2.5 Synthesis of Silver Nanoparticles

From a chemical viewpoint, the synthesis of nanoparticles in solution (colloidal solution) requires the use of methods allowing a precise control over the size and the shape of the nanoparticles to yield a set of monodisperse nanoparticles displaying a specific property. In general, the synthesis of metal nanoparticles in solution is carried out by the use of the following components: i) metal precursor; ii) reducing agent and iii) stabilizing agent. The mechanism of formation of colloidal solutions from the reduction of silver(I) ions consists of two stages: nucleation and growth. The nucleation step requires high activation energy while the growing step requires low activation energy. The size and the shape of the nanoparticles will depend on the relative rates of these processes that can be controlled through the adjustment of the reaction parameters (concentration, temperature, pH, reducing ability, *etc*.) [38]. In the case of silver nanoparticles, the first described methods are the Lee-Meisel [39] and the Creighton method [40]. The former consists of a modification of the Turkevich method for the synthesis of gold nanoparticles using $AgNO_3$ instead of $HAuCl_4$ as metallic precursor and sodium citrate as the reducing agent. In this method the obtained nanoparticles display a broad size distribution. The Creighton method consists of the reduction of $AgNO_3$ with $NaBH_4$ as the reducing agent. This is the most popular method and can generate Ag NPs of 10 nm and showing a narrow size distribution. Based on the above mentioned methods, a variety of chemical reactions that allow the synthesis of Ag NPs by chemical reduction of a silver salt have been described. In this type of reactions the oxidation of the formed nanoparticles is not thermodynamically favored due to the high reduction potential of silver, which permits the aqueous or alcoholic suspensions without the presence of stabilizing agents. In addition, the double electric layers formed around the nanoparticles in colloidal solutions of low ionic strength inhibit the aggregation of the nanoparticles. In the case of colloidal solutions of high ionic strength or in organic phase, the use of stabilizing agents acting

as self-assembled monolayers, surfactants, polymers or dendrimers is needed. These agents not only protect the nanoparticles from the environment and prevent their agglomeration, but also play an important role in the size and shape control. The methods by which nanoparticles are synthesized by the reaction between a metallic salt and chemical reducing agents are the most versatile ones. Among them, it is worth mentioning the formation of Ag NPs from $AgNO_3$ and using soft reducing agents as ascorbic acid, polyols or monosaccharides. In the case of ascorbic acid acting as reducing agent, the change in the reaction conditions allows the synthesis of silver nanoparticles of large size (upto 1200 nm).

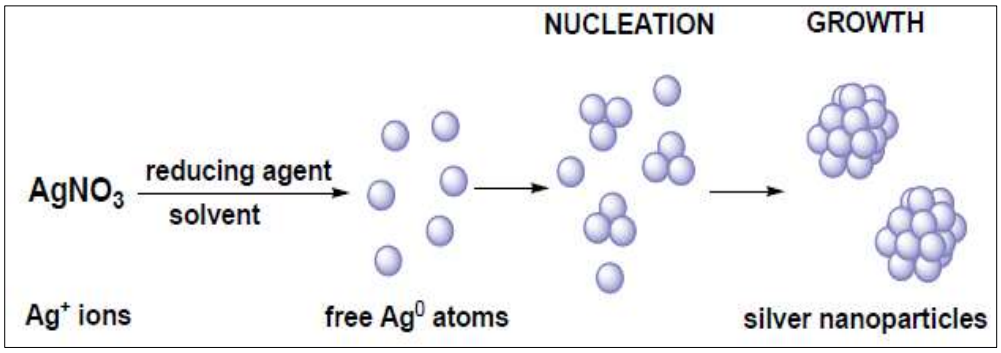

Figure 2.3: Formation of silver nanoparticles

2.6 Reduction Methods of Silver Nitrate

Precious metal nanoparticles distributed in a dielectric matrix have attracted attention of many researchers from both theoretical and practical stand points. Such nanocomposites exhibit unique optical and electrical properties, which make them promising materials for new sensors, optoelectronics, nonlinear optics, catalytic applications, energy storage, and so on. Polymers are now often considered as a dielectric matrix for a nanocomposite. For a practical application, nanoparticles should have a size of 5–30 nm and should be uniformly distributed in the dielectric volume. Unfortunately, metal nanoparticles tend to join into large clusters because of a high surface reactivity. The composites produced by mechanical mixing of metal nanoparticles with molten polymers usually have a strongly heterogeneous structure. Researchers use many other methods to fabricate metallic nanocomposites, including simultaneous evaporation and sputtering of metals and polymers and implantation of silver ions into polymers. One of the approaches uses in situ polymerization, which

includes the dissolution and reduction of salts or metal complexes along with the polymerization of an initial monomer [41].

Since past several years nanosized metallic particles, especially silver nanoparticles impregnated with polymer matrix have been synthesized successfully by various research groups using various synthetic techniques [42 – 47]. The polymers can acts as a stabilizer in such system, and its role is to prevent the further growth and aggregation of silver nanoparticles. Silver is particularly attractive among metal nanoparticles because of its significance widespread applications in biology, antimicrobial properties, optical properties, and oxidative catalysis. There are many research literature reported on the synthesis of silver nanoparticles from Ag ions. Few of them are chemical reduction using aqueous solution of sodium borohydride ($NaBH_4$), hydrazinium hydroxide (N_2H_4OH), dimethyl formamide (DMF), photoreduction by UV irradiation, and simple heat treatment. DMF is essentially used as a solvent and is also able to reduce Ag ions to the metallic silver even at room temperature and in the absence of any external reducing agent. The reduction of silver ion into silver metallic nanoparticles could be performed by three different techniques such as chemical reduction using $NaBH_4$, heat treatment and refluxed the PAN/DMF solutions containing $AgNO_3$ at 80 °C for 2 h prior to electrospinning[42].

UV assisted polymerization is of deep interest. This method of synthesizing nanocomposites is characterized by low temperatures and a high polymerization rate, which leads to the formation of uniformly distributed metal nanoparticles during the growth of a polymer network without using additional solvents and reducing agents. Moreover, such nanomaterials are characterized by a simple and inexpensive process of production. The radicals formed by UV are electron donors and can simultaneously polymerize monomers and reduce metal salts, which, in turn, form metallic nanoparticles [41].

Silver has been a material of great interest as it has the highest electrical and thermal conductivity among the metals. Polymer composites with silver nanoparticles are receiving considerable attention due to numerous solid state potential applications in many fields, e.g. organic electronics, catalysts, plasmonics, coatings, antimicrobials, etc. UV-curing is a well established polymerization technique that takes place upon

UV irradiation to obtain a highly cross-linked 3D polymer network. The process is well known for being fast and environmentally friendly [48].

In fact, UV photochemically assisted polymerizations are characterized by low temperature conditions and faster polymerization rates, resulting in the formation, during the polymer network growth, of homogeneously dispersed metal nanoparticles without the use of further solvents and reducing agents. The UV photochemically generated radicals, being electron donor species, are able to simultaneously polymerize monomers and reduce the metal salts, which will form metal nanoparticles [49].

Radiation technology has been used widely in the modification of polymeric materials for many years. Ionizing radiation can induce various phenomena in polymers, such as promoting chain branching to cross linking and chains on to degradation. Crosslinking and degradation processes occur simultaneously, and the dominating process is determined by thetreatment conditions and the intrinsic polymer properties. Crosslinking improves materials properties, such as thermal stability, and strength while chain scission induces damage. In the presence of oxygen, radiation oxidation occurs in any polymer, and leads to chain scission, which is associated with remarkable changes in the mechanical properties of the starting materials. The extent of radiation oxidation in a polymer material is dependent on the radiation conditions, such as dose, dose rate, oxygen pressure,and irradiation temperature,as well as the structure of the polymer. Polyacrylonitrile (PAN) has been found to be crosslinkable by gammaradiation in vacuum, but chain scission is the main reaction in the presence of oxygen. PAN fiber is known to be the main precursor of carbon .

Ag nanoparticles in PAN nanofibrous film can be obtained by chemical reduction of $AgNO_3$ for 30 min in N_2H_5OH aqueous solution. Electrospinning og Ag/PAN nanofibers after storing the $AgNO_3$/PAN solution in N,N-dimethylformamide (DMF) for 10 days at room temperature was done. DMF is reported to be able to reduce Ag^{+1} ions to the zero-valent metal, even in the absence of any external reducing agent. This spontaneous reduction of Ag^{+1} ions in DMF without a protecting agent leads to the homogeneous deposition of silver nanoparticles on clean glass surfaces in contact with the solution [50].

Ag nanoparticles dispersed in PAN nanofibrous film were prepared by reduction of silver nitrate in N_2H_5OH aqueous solution as follows. In a 50 ml beaker was a piece of 10x20 mm^2 $AgNO_3$/PAN nanofibrous film, 20 ml tripled distilled water and 1 ml N_2H_5OH were mixed in the beaker. The silver ions in PAN nanofibrous film were reduced to silver at room temperature. Thirty minutes later, the film was taken out to wash with distilled water and alcohol. Then it was dried in a vacuum oven [46,51]. They electrospun a PAN/DMF solution that contained silver ions into nanofibers and then reduced the silver ions on the nanofibers by hydrazine hydroxide [45,46,52].

A xenon arc lamp is a specialized type of gas discharge lamp, an electric light that produces light by passing electricity through ionized xenon gas at high pressure. It produces a bright white light that closely mimics natural sunlight. Xenon arc lamps are used in movie projectors in theaters, in search lights, and for specialized uses in industry and research to simulate sunlight. Xenon head lamps in automobiles actually use metal-halide lamps where a xenon arc is only used during start-up. Xenon short-arc lamps were invented in the 1940s in Germany and introduced in 1951 by Osram. First launched in the 2 kW size (XBO2001), these lamps saw wide use in movie projection, where they replaced the older, more complicated carbon arc lamps. The white continuous light generated by the xenon arc is spectrally similar to daylight, but the lamp has a rather low efficiency in terms of lumens of visible light output per watt of input power. Today, almost all movie projectors in theaters employ these lamps, with power ratings ranging from 900 watts up to 2 kW [53].

Exposure to sunlight is known to have a degradative effect on most natural fibers. Such exposure can cause loss of strength and extensibility, discoloration, fading, and disintegration of fabrics. This problem has not been overcome with the development of synthetic polymeric materials, as many of them are also damaged by sunlight [53].

High-energy radiation may be classified into photon and particulate radiation. Gamma radiation is utilized for fundamental studies and for low-dose rate irradiations with deep penetration. The radioactive isotopes, cobalt-60 are the main sources of gamma radiation. Lower energy x-radiation is produced by electron bombardment of suitable metal targets with electron beams, or in a synchrotron. Electron irradiation is normally obtained from electron accelerators to give beams with energies in the MeV range. The corresponding penetration depths are in the mm range. Much lower energy electron

beams, e.g. 10-20 keV, are used in electron microscopy and in electron-beam lithography. In these cases, a large proportion of the energy is deposited in thick polymer films. Nuclear reactors are a source of high radiation fluxes comprised mainly of neutrons and gamma rays, and large ionized particles (fission products) close to the fuel elements. The neutrons largely produce protons in hydrocarbon polymers by Hknock-onM reactions, thus, the radiation chemistry of neutrons is similar to that of proton beams, which may alternatively be produced using positive-ion accelerators. Classical sources for ultraviolet radiation include mercury and xenon arc lamps, which have the advantage of broad band excitation for spectroscopic studies, but suffer from the corresponding broad monochromator controlled band width. Excimer laser sources provide intense coherent radiation in the deep ultraviolet region. Finally, synchrotron sources provide a broad range of radiation energy, including the deep ultraviolet. Absorption of high-energy radiation by polymers produces excitation and ionization and it is these excited and ionized species that are the initial chemical reactants. The ejected electron must lose energy until it reaches thermal energy. Geminate recombination with the parent cation radical may then occur and is more likely in substrates of low dielectric constant. The resultant excited molecule may undergo homolytic or heterolytic bond scission. Alternatively, the parent cation radical may undergo spontaneous decomposition, or ion-molecule reactions. The initially ejected electron may be stabilized by interaction with polar groups, as a solvated species or as an anion radical. The radiation chemistry taking place within a polymeric material is, thus, quite complicated, involving chemistry of neutral, cation and anion radicals, cations and anions, and excited species. Although the absorption of radiation energy is dependent only on the electron density of the substrate and, therefore, occurs spatially at random on a molecular scale, the subsequent chemical changes are not random. Some chemical bonds and groups are particularly sensitive to radiation-induced reactions. They include COOH, C-X where X=halogen, -S02-, NH2 , and C=C. Spatial specificity of chemical reactions may result from intramolecular or intermolecular migration of energy or reactive species such as free radicals or ions. Enhanced radiation sensitivity may be designed into polymer molecules by incorporation of radiation sensitive groups as in lithographic materials. Aromatic groups have long been known to give significant radiation resistance to organic molecules.

A substantial intramolecular protective effect by phenyl groups in polymers is demonstrated by the low G values for H 2 formation and crosslinking in polystyrene (substituent phenyl), polyarylene sulfones (backbone phenyl), as well as many other aromatic polymers. While the relative radiation resistance of different aromatic groups in polymers has not been extensively studied, most aromatic substituents afford similar protection. It has been observed, however, that biphenyl and phenolic moieties provide increased radiation resistance to polymer materials relative to other aromatic groups. In one example, it was demonstrated that the phenolic group in tyrosine protects the radiation sensitive carboxylic acid groups of glutamic acid even though tyrosine itself may undergo crosslinking to a greater extent than would phenylalanine. The molecular changes occurring in polymers as a result of radiation-induced chemical reactions may be classified as i) chain crosslinking effecting an increase in molecular weight and formation of a macroscopic network (polymer solubility decreases with increased radiation dose); ii) chain scission effecting a decrease in molecular weight and, thus, substantially changing a polymer materials properties (strength, both tensile and flexural, decreases, and the rate of dissolution in a given solvent increases). In addition to these changes, irradiation of polymers will frequently give rise to small molecule products, resulting from bond scission followed by abstraction or combination reactions [54].

2.7 Poly(N-vinylpyrrolidone)

It was in late 1930s' that Professor Walter Reppe of BASF first invented and patented the polymer, PVP. In the more then 70 years since that significant milestone, we have been continuously advancing its development to further its applications. Originally used as a plasma substitute, PVP was introduced to a wide variety of applications in pharmacy, cosmetics and industrial production.

The PVP grades can be used in suspensions, dry granulates, and dry syrups as physical stabilizers. The most important function of these hydrophylic polymers in such cases is as a protective colloid; the individual solid particles are rendered hydrophylic and separated sterically. In this way, dispersibility is improved and the sediment volume can be increased. A further general function of PVP is that it can prevent crystallization of the dissolved active substance by forming soluble complexes with it [55].

Polyvinyl pyrrolidone (PVP) is an amorphous polymer, which can permit faster ionic mobility compared to other semicrystalline polymers and has low scattering loss, which make sit an ideal polymer for blend based materials for optical applications. Second, due to the presence of carbonyl group in the side chains of PVP, it forms a variety of complexes with various in organic salts. It interacts well with severalty pesofions and enhances the number of free ions in the system. Another advantage of using PVP is that it can be thermally crosslinked, resulting in out standing thermal stability and mechanical strength of the blend material.

Usually stabilizers are required to obtain stable, monodispersed nanoparticles. They are used to protect the particles from the aggregation and in their presence the probability of nanoparticles collision and coalescence decreases due to the reaction between functional groups of the stabilizer and nanoparticle. Therefore, silver-silver nanoparticle bonds do not form and agglomeration is enhanced by formation of the stabilizing agent layer on the surface of nanoparticles. PVP is a homopolymer with a polyvinyl backbone and its repeating units contain a highly polar amide group that confers hydrophilic and polar-attracting properties, and also non-polar methylene groups both in the backbone and in the ring that confer hydrophobic properties. The N and O in the polar groups have a strong affinity for silver ions and silver nanoparticles [56]. In general, the PVP protective mechanism is divided into three stages. The first stage involves the formation of coordinative bonding between the stabilizer and silver ions - PVP donates a lone pair of electrons of oxygen and nitrogen to sp orbitals of silver ions. Secondly, the formed complex promotes silver nucleation which leads to the aggregation of silver atoms.

The incorporation of metal nanoparticles into polymer nanofibers can be achieved using either electrospinning polymer solutions containing metal nanoparticles or by reducing the metal salts or complexes in the electrospun polymer nanofibers. In practice, polymer nanofibers containing Ag nanoparticles can be prepared using polymers with a strong interaction with Ag nanoparticles. Poly(N-vinylpyrrolidone) (PVP) has attracted a great deal of attention as a polymer that can stabilize Ag nanoparticles.

Poly(N-vinylpyrrolidone) (PVP) was used in two methods to prepare polymer nanofibers containing Ag nanoparticles. The first method involved electrospinning the

PVP nanofibers containing Ag nanoparticles directly from the PVP solutions containing the Ag nanoparticles. N,N-Dimethylformamide was used as a solvent for the PVP as well as a reducing agent for the Ag ions in the PVP solutions. PVP containing Ag nanoparticles could be used to introduce Ag nanoparticles to other polymer nanofibers that are miscible with PVP. This means that PVP not only promotes the nucleation of Ag nanoparticles but also prohibits their aggregation [57].

2.8 Antimicrobial Efficiency

As it has been mentioned in the introduction section the antimicrobial effect of silver salts is well known since the 19th century. In the studies carried out in the last years, silver was defined as "oligodynamic" due to its ability to produce a bactericidal effect at very low concentrations [34]. This feature of Ag+ ions arises from its high affinity towards proteins, enzymes, DNA, RNA, *etc*. due to the interactions with functional groups such as thiol, carboxylate, phosphate, hydroxyl, imidazole, indole or amines what can interfere in microbial processes. During the last years a tremendous effort has been carried out on the synthesis of these new silver-based nanomaterials, especially focused on the development of new or enhanced antibacterial properties.

Bactericidal coatings based on Ag nanoparticles deposited on TiO_2 films are an important class of biomaterials due to their application in surgical implant procedures. These multifunctional materials display interesting properties such as antimicrobial activity and biological compatibility. The synthetic approaches for the synthesis of Ag-TiO_2 composites are varied, for example, from simple reduction of Ag+ ions by $NaBH_4$ in the presence of a suspension of TiO_2 to more complex ones such us the photoreduction of $AgNO_3$ in the presence of PVA capped TiO_2 nanoparticles/nanotubes. Another emerging class of antibacterial hybrid inorganic nanocomposites is Ag-hydroxyapatite nanomaterials because of their use in industrial and medical applications. Recent results include the preparation of antibacterial silverhydroxyapatite by the reduction of silver ions by hydroxyl groups at the surface of hydroxyapatite leading to needle like silver nanoparticles [34].

Carbon-based nanomaterials such as carbon nanotubes or graphene display unique physical and chemical properties. The combination of these carbon-based

nanomaterials with silver nanoparticles constitutes an interesting class of antibacterial materials. Ag-chemically converted graphene nanocomposite was prepared through a chemical reduction of graphene oxide. This nanocomposite display antibacterial properties against several microorganisms. Also, the synthesis and study of antibacterial properties of silver coated carbon nanotubes were carried out. This nanocomposite was prepared through the chemical reduction of silver (I) acetate with dimethylformamide, in the presence of carbon nanotubes and displayed good antibacterial activity against different microorganisms such as *Staphylococcus aureus*, *Streptococcus pyogenes, Escherichia coli* and *Salmonella enteric*.

Ag NPs can be currently synthesized through different types of chemical methods in solution, allowing the design of silver-based nanomaterials of different size and shape or with specific coatings. This synthetic versatility makes these nanoparticles very attractive for potential practical applications. Thus, the bactericidal properties displayed by silver nanoparticles are a very active research field, not only because of the applications that can be derived, but also because the mechanism of action is still a matter of intense research.

3. EXPERIMENTAL PART

3.1 Materials

Polyacrylonitrile (PAN), (Mw = 150000 g/mol), and poly(N-vinylpyrrolidone) (PVP) (Mw = 360000 g/mol) were obtained from Sigma Aldrich. N,N-Dimethylformamide (DMF) and hydrazinium hydroxide (N2H5OH) were obtained from Merck. Silver nitrate (AgNO3) with 99.9995 % purity was obtained from Alfa Aesar Premion.

Hydrazine hydroxide (N_2H_5OH) was used for the chemical reduction of silver nitrare. Chemicals were analytical grade and were used without further purification.

3.2 Equipments

3.2.1 Electrospinning device

The formation of the silver nitrate loaded PAN nanofibers occured in the electrospinning system. In the electrospinning system, the composite polymer solution which is loaded into a syringe was purged to the needle tip by the syringe pump. A positive voltage was applied to the rotating drum collector that covered with aluminum foil and the negative voltage from high-voltage power supply was connected to the needle tip. Nanofiber web is collected on nonwoven mat covered on the aluminum foil due to high electric field. On electrospinning system, the feeding rate of the polymer solutions was 1 mL/h with 15 kV electrospinning voltage and the distance between the needle tip and collector was 10 cm.

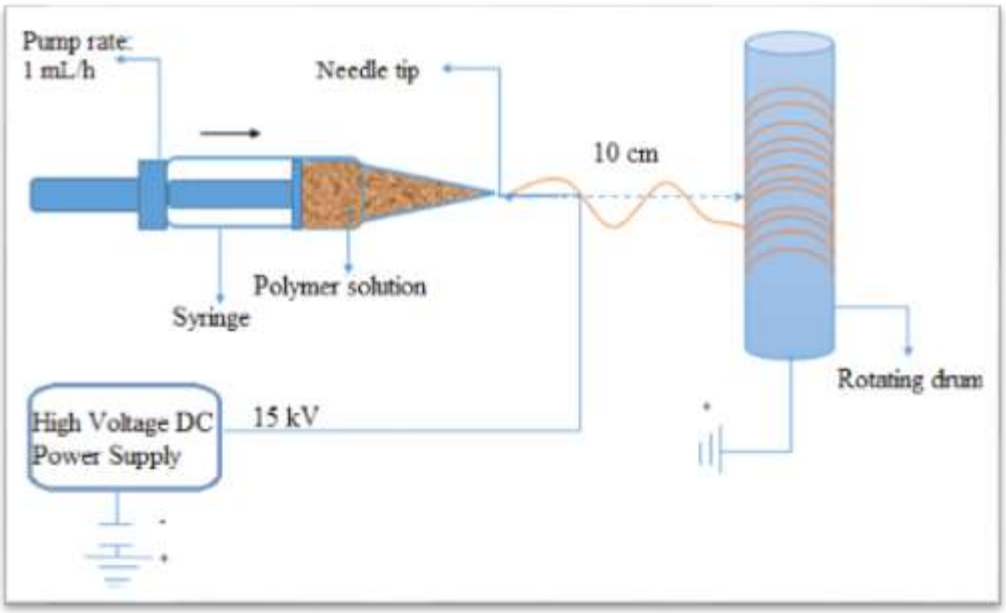

Figure 3.1 : Electrospinning system [58].

3.2.2 Conductometer

Microtest LCR Meter 6370 (0.01 mΩ-100 MΩ) with two circular probe with four wire system was used for the measurement of the resistance of composite nanofibers. Electrical conductivity values was carried out under the standard atmospheric conditions (20 ±2 ºC, 65% ±5 Rh).

3.2.3 Tensile loading machine

Tensile tester was used for the evaluation of mechanical properties of nanofibers such as modulus, tensile strength and elongation at break.

3.2.4 UV- visible spectroscopy

UV-1700 Pharmaspec UV-Visible Shimadzu spectrophotometer was used for obtaining the UV-Vis. spectra of solutions.

3.2.5 Scanning electron microscopy (SEM)

The morphology and the structure of the reduced composite nanofibers were investigated by SEM Carl Zeiss EVO MA10 type scanning electron microscope.

3.2.6 Differential scanning salorimetry (DSC)

TA DSC Q10 type differential scanning calorimetry was used for thermal analysis at a heating rate of 20 ˚C/min under nitrogen atmosphere (temperature range between 30-350 ˚C).

3.2.7 X-ray differaction (XRD)

The crystallinity of the samples was investigated by X-ray diffraction analysis. Bruker® AXS D8 Advance X-ray diffractometer system was used to obtain wide-angle X-ray diffraction traces, under the conditions of 40 kV voltage and 40 mA current. The observed equatorial X-ray scattering data was collected in reflection mode in the 5-40º 2θ range.

3.2.8 Antimicrobial efficiency test

Antimicrobial test against bacteria *Staphylococcus aureus* for 24 h was carried out according to ASTM E2149-10 standard. The efficiency test were done in the Ege University Faculty and Science Biology Department.

3.3 Preparation of Silver Nitrate Loaded Solutions

In the first stage of the study, the most effective reduction method was determined. For this purpose 10 wt % $AgNO_3$ loaded polymer solutions were prepared and different reduction methods were applied. The abbraviations of reduction methods are listed in the Table 3.1. The flowchart of the applied reduction methods can be seen from the Figure 3.2.

Table 3.1 : Abbreviations of reduction methods.

Full Name of Applied Reduction Method	**Abbreviations**
Reduction of the composite solution by UV-light	UV-light method
Reduction of composite nanofiber by hydrazine hydroxide solution	Hydrazine method
Reduction of the polymer composite solution by xenon arc lamp	Xenon-solution
Reduction of the composite nanofiber by xenon arc lamp	Xenon-web method
Reduction of the polymer solution by reflux technique	Reflux method

PAN, DMF and $AgNO_3$ were used to prepare composite nanofibers or nanofiber solutions. Polyacrylonitrile (PAN) was dissolved in DMF to prepare solutions with a concentration of 7 wt % and 10 wt % $AgNO_3$ (the weight percentage of $AgNO_3$ in the solution was calculated on the basis of PAN weight, i.e., the ratio of $AgNO_3$ to PAN is 10%) was then added into the solutions.

PAN (7 wt%) was dissolved in DMF at 60 °C, 400 rpm for 1.5 h, then 10 wt% $AgNO_3$ was added to solution and stirred for 1 h at 400 rpm. The bakers that contain silver composite solutions were covered with an aluminum foil to prevent from undesirable effects of direct sunlight.

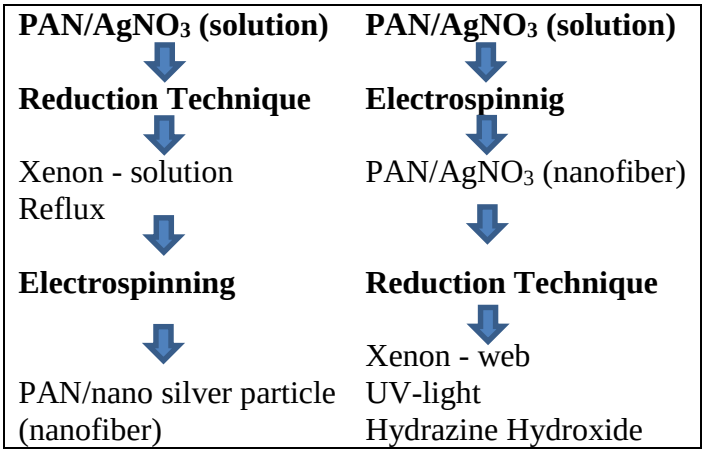

Figure 3.2 : Flowchart of the reduction methods

$AgNO_3$ was reduced into silver metallic nano particles by applying five different techniques (Hydrazine, Reflux, Xenon-sol, Xenon-web and UV-light). The chemical reduction by the hydrazine hydroxide was performed in the presence of an aqueous solution using distilled water/hydrazine hydroxide volume ratio (20:1). After the electrospinning process, the nanofibers were laid into an aqueous solution for 30 min, afterwards washed with distilled water two times, dried in an oven at 40 °C for 2 h and then kept 2 days at room temperature.

Reduction by reflux method was applied at 80 °C using water bath for 2 h by stirring with 400 rpm. It was observed that the color of the composite solution turned into yellow and to light-brown.

In the Xenon-sol method, Suntest CPS Heraeus Original Hanau Xenon Strahler Xenon Lamp was used to irradiate the composite solution with the photo intensity adjusted to

4 for 30 min. After reduction of composite solution, electrospinning was done. Xenon-web method was applied for the composite nanofiber which is not reduced before, for 30 min by Xenon arc adjusted to 4 photo intensity in order to obtain reduced nanofiber.

In the case of UV-light method, A. Krüss Optronic UV 240 machine was used. The intensity of the lamp was adjusted to a scale of 2 [58].

In the next step of the study, PVP loaded samples were produced to see the effects of different loadings of PVP on desired properties. The weight ratio of PVP to $AgNO_3$ was adjusted to 7:1 and 1:1 (PVP/$AgNO_3$). PVP is dissolved in PAN/DMF solution and then, 10% $AgNO_3$ was loaded.

The other stage of the study was the determination of dispersion technique. In this dispersion method, $AgNO_3$ was added to the solvent (DMF) and mixed for 10 min by ultrasonic homogenizer, then for 45 min by an ultrasonic bath. Then polyacrylonitrile was added into thesolution and mixed by magnetic mixer until PAN dissolved. The electrospinning of the final solution was prepared using the same conditions as mentioned before. [51].

The next step of the study was the determination of the most affective ratio of silver nitrate loading. So that, different ratio (1 wt%, 3 wt%) of silver nitrate was included into the polymer solutions.

3.4 Analyses

3.4.1 Conductivity measurements

Microtest LCR Meter 6370 (0.01 mΩ-100 MΩ) with two circular probe with four wire system was used for the measurement of the resistance of composite nanofibers. The thicknesses of the samples were measured with the integrated thickness meter. At least 7 measurements were done to obtain average value of electrical conductivity and thickness of nanofiber web. Volume conductivity of the samples in S/cm were calculated according to equation 1 as indicated in ASTM standards [59, 60]. Volume resistance values were measured and the conductivity of the composite nanofibers in S/cm were calculated by the use of geometric dimensions of the samples.

$$\gamma_v = t /(A x R_v) \quad \textbf{(1)}$$

where:

R_v = volume resistance, Ω,

A = area of the electrodes, cm^2 and

t = distance between the electrodes, cm.

The results are given in the section 4.1.

3.4.2 Tensile test

Tensile tester was used for the evaluation of mechanical properties of nanofibers such as modulus, tensile strength and elongation at break. Breaking strength, breaking elongation and modulus of the webs were obtained with a 100N load cell at a crosshead speed of 20 mm/min. The gage length was 15 mm and specimens were cut in 35 mm (length) x 5 mm (width) dimensions for tensile testing. At least seven samples were used to obtain average values of mechanical properties. The thicknesses of the specimens were measured with a Mitutoyo digital micrometer. The results are given in the section 4.2.

3.4.3 UV-visible spectra

UV-1700 Pharmaspec UV-Visible Shimadzu spectrophotometer was used for obtaining the UV-Vis. spectra of solutions containing PVP and nanofibers reduced by different methods. The measurements were carried out at room temperature with a 1 cm quartz cell within the 200 to 600 nm.

Ultraviolet–visible spectroscopy or ultraviolet-visible spectrophotometry (UV-Vis) refers to absorption spectroscopyor reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared [NIR]) ranges. The absorption or reflectance in the visible range directly affects the perceived color of the chemicals involved. In this region of the electromagnetic spectrum, molecules undergo electronic transitions. This technique is complementary to fluorescence spectroscopy, in that fluorescence deals with transitions from the excited state to the ground state, while absorption measures transitions from the ground state to the excited state. The results are given in the section 4.3.

3.4.4 Scanning electron microscopy (SEM) images

The morphology and the structure of the reduced composite nanofibers were investigated by SEM Carl Zeiss EVO MA10 type scanning electron microscope. The SEM observations were performed at 5 kV voltages. Samples were coated with a gold conductive surface to prevent charging effects. The diameter of the nanofibers was measured on SEM photomicrographs and analyzed using the Image J Software. At least 50 measurements were done to obtain average fiber diameter.

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image. SEM can achieve resolution better than 1 nanometer. Specimens can be observed in high vacuum, in low vacuum, in wet conditions (in environmental SEM), and at a wide range of cryogenic or elevated temperatures.

The most common mode of detection is by secondary electrons emitted by atoms excited by the electron beam. On a flat surface, the plume of secondary electrons are mostly contained by the sample, but on a tilted surface, the plume is partially exposed and more electrons are emitted. By scanning the sample and detecting the secondary electrons, an image displaying the topography of the surface is created. The results are given in the section 4.4.

3.4.5 Differential scanning calorimetry (DSC)

Differential scanning calorimetry or DSC is a thermo-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. Both the sample and reference are maintained at nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned.

TA DSC Q10 type differential scanning calorimetry was used for thermal analysis of different silver nitrate loaded, different PVP loaded nanofibers. And also the effect of reduction methods on thermal stability of the nanofibers was investigated. The results are given in the section 4.5.

3.4.6 X-ray differaction (XRD)

The crystallinity of the samples was investigated by X-ray diffraction analysis. Bruker® AXS D8 Advance X-ray diffractometer system was used to obtain wide-angle X-ray diffraction traces, under the conditions of 40 kV voltage and 40 mA current. The observed equatorial X-ray scattering data was collected in reflection mode in the 5-40º 2θ range. The results are given in the section 4.6.

3.4.7 Antimicrobial efficiency test

Antimicrobial test against bacteria Staphylococcus aureus for 24 h was carried out according to ASTM E2149-10 standard. The effect of the silver nitrate amount on the antimicrobial efficiency was investigated. The results are given in the section 4.7.

3.4.8 Yellowness comparison

After reduction of the silver nitrate the color change. The effective use of the nanofibers in the industry sometimes could be related with the color of nanofibers. Yellowness sometimes is not required results such as wound healing and air or water filtration systems. The comparison was made by eye detection. The results are given in the section 4.8.

3. 5 Preparation of Formulations

Different formulations and reduction methods were studied to improve the conductivity of produced nanofibers.

Table 3.2 : Sample codes of 10 % silver nitrate loaded nanofibers reduced bydifferent reduction methods.

Sample	**Silver Content**	**Reduction Method**	**Final name of samples**
PAN	-	-	-
PANSNp	10 %	-	PANSNp
PANSNp	10 %	Reflux	PANSNp-10-Reflux
PANSNp	10 %	Xenon-sol	PANSNp-10- Xenon-sol
PANSNp	10 %	Xenon-web	PANSNp-10- Xenon-web
PANSNp	10 %	Hydrazine	PANSNp-10- Hydrazine

Table 3.3 : Sample codes of different dispersion methods applied on different amount of silver nitrate loaded nanofibers reduced by hydrazine method.

Sample	Silver Content	Reduction Method	Dispersion method	Final name of samples
PANSNp	1 %	Hydrazine	Magnetic stirrer	PANSNp-1-Hydrazine-Magnetic
PANSNp	1 %	Hydrazine	Ultrasonic bath	PANSNp-1-Hydrazine-Ultrasonic
PANSNp	3 %	Hydrazine	Magnetic stirrer	PANSNp-3-Hydrazine-Magnetic
PANSNp	3 %	Hydrazine	Ultrasonic bath	PANSNp-3-Hydrazine-Ultrasonic
PANSNp	10 %	Hydrazine	Magnetic stirrer	PANSNp-10-Hydrazine-Magnetic
PANSNp	10 %	Hydrazine	Ultrasonic bath	PANSNp-10-Hydrazine-Ultrasonic

Table 3.4 : The effect of PVP ratio on electrical conductivity.

Sample	Silver Content	Reduction Method	PVP Ratio	Final name of samples
PANSNp	10 %	Hydrazine	-	PANSNp-10-Hydrazine
PANSNp	10 %	Xenon-sol	-	PANSNp-10-Xenon-sol
PANSNp	10 %	Hydrazine	1:1	PANSNp-10-Hydrazine-1PVP
PANSNp	10 %	Hydrazine	7:1	PANSNp-10-Hydrazine-7PVP
PANSNp	10 %	Xenon-sol	7:1	PANSNp-10-Xenon-sol-7PVP

To improve the mechanical properties, different amount of silver nitrate loading and two types of dispersion methods were used.

4. RESULTS AND DISCUSSIONS

4.1 Conductivity

It can be said from the Table 4.1 that the best reduction method for obtaining higher electrical conductivity is obtained by the samples reduced by the hydrazine method and the arc-web method.

Table 4.1 : Electrical conductivity results of 10 % silver nitrate loaded nanofibers reduced by different reduction methods.

Samples	Electrical Conductivity (S/cm)	CV %
PANSNp-10-Reflux	7.85×10^{-8}	18.6
PANSNp-10- Xenon-sol	4.86×10^{-8}	24.5
PANSNp-10- Xenon-web	1.82×10^{-7}	13.2
PANSNp-10- Hydrazine	1.39×10^{-7}	28.9

The higher electrical conductivity values may be obtained from the higher amount of silver nano particles that available on the nanofiber surface. Hydrazine and Xenon-web methods provide surface reduction of silver nano particles. So that the electrical conductivity is higher than the other methods.

Table 4.2 : Effect of dispersion method on different amount of silver nitrate loaded nanofibers reduced by hydrazine method.

Samples	Electrical Conductivity (S/cm)	CV %
PANSNp-1-Hydrazine-Magnetic	3.65×10^{-8}	30.9
PANSNp-1-Hydrazine-Ultrasonic	3.61x10-^{7}	15.6
PANSNp-3-Hydrazine-Magnetic	1.36×10^{-7}	22.5
PANSNp-3-Hydrazine-Ultrasonic	3.55x10-^{7}	26.5
PANSNp-10-Hydrazine-Magnetic	1.39×10^{-7}	28.9
PANSNp-10-Hydrazine-Ultrasonic	4.86×10^{-8}	26.5

The amount of reduced silver nano particles may vary between the outer surface and the inner region of the nanofiber web, especially when the arc-web and the hydrazine

nanoweb reduction methods are considered. To improve the electrical conductivity of nanofibers, different dispersion techniques were applied to the polymer solution.

Table 4.3 shows the different ratio of PVP loading effect on the electrical conductivity of nanofibers. Due to the polar groups of PVP, silver nano particles form coordination bonds with the PVP. The layers cover the surface of the silver nano particles [61]. The PVP loading disturbs the electrical conductivity networks and causes a decrease in the electrical conductivity.

Table 4.3 : Effect of PVP on electrical conductivity of 10 % silver nitrate loaded nanofibers reduced by different reduction methods.

Samples	Electrical Conductivity (S/cm)	CV %
PANSNp-10-Hydrazine	1.39×10^{-7}	28.9
PANSNp-10-Xenon-sol	4.86×10^{-8}	24.5
PANSNp-10-Hydrazine-1PVP	5.88×10^{-9}	28.1
PANSNp-10-Hydrazine-7PVP	1.02×10^{-8}	32.9
PANSNp-10-Xenon-sol-7PVP	1.81×10^{-9}	35.9

4.2 Tensile Test

As seen from Table 4.4, the strength of the 100% PAN increases when it is treated with hydrazine hydroxide.

Table 4.4 : Effect of dispersion method and amount of silver nitrate loading on mechanical behavior of nanofibers.

Samples	Tensile Strength (N/mm^2)	CV %	Tensile Strain (%)	CV %	Modulus (N/mm^2)	CV %
PAN	1.56	14.5	17.24	13.9	12.64	13.9
PAN-Hydrazine	2.14	30.7	15.69	19.6	5.80	22.6
PAN-Xenon-sol	1.20	13.2	15.94	27.4	7.75	30.2
PANSNP-1-Magnetic	1.83	19.2	9.85	17.3	5.38	29.5
PANSNp-1-Hydrazine-Magnetic	2.67	20.8	14.09	11.3	5.26	32.2
PANSNp-1-Hydrazine-Ultrasonic	2.54	13.6	16.19	14.7	12.75	31.6
PANSNP-3-Magnetic	1.27	30.0	10.59	16.9	6.85	28.1
PANSNp-3-Hydrazine-Magnetic	1.27	28.1	16.22	25.1	3.23	26.3
PANSNp-3-Hydrazine-Ultrasonic	2.33	11.5	12.43	25.3	13.78	27.0
PANSNp-10-Magnetic	1.34	25.4	19.56	17.3	14.09	24.3
PANSNp-10-HydrazineMagnetic	1.98	25.0	19.93	6.7	10.64	27.6
PANSNp-10-Hydrzine-Ultrasonic	1.24	29.3	17.21	23.2	12.28	31.7

It has been seen that hydrazine treatment results to more compact structure due to dimensional shrinkage of nanofiber web. Thus this compactness can also cause an increase in strength of nanofiber web treated by hydrazine hydroxide.

Hydrazine method may also form crosslinking between PAN chains leading to an increased tensile strength [46]. The higher breaking strength values was obtained from 1% $AgNO_3$ loaded nanofiber due to less agglomeration tendency compared to the others.

As seen from the Table 4.5, reduction in solution before the production of nanofiber web may have higher risk for the agglomeration of silver nano particles.

Table 4.5 : Effect of reduction method on mechanical behavior of nanofibers.

Samples	Tensile Strength (N/mm^2)	CV %	Tensile Strain (%)	CV%	Modulus (N/mm^2)	CV%
PAN	1.56	14.58	17.24	13.97	12.64	13.98
PANSNp-10-Reflux	1.71	28.53	7.60	17.74	4.44	32.57
PANSNp-10- Hydrazine	1.98	25.02	19.93	6.78	10.64	27.65
PANSNp-10- Xenon-sol	1.24	29.29	17.21	23.23	12.28	31.7
PANSNp-10- Xenon-web	1.54	20.62	19.58	37.96	9.81	39.73

The agglomeration of silver nano particles generally affects negatively the properties of composite material. Xenon-sol method may also cause degradation of the polymer in solution [58]. Thus, composite nanofibers reduced by arc-sol method resulted with the lowest breaking strength values.

As seen from the Table 4.6, low ratio of PVP (1:1 PVP) provides better improvement on the strength of composite PAN nanofiber. It is known that higher ratio of PVP (7:1 PVP) is not sufficient to prevent agglomeration of nano particles because of the optimum concentration is exceeded.

It can be concluded from the Table 4.6 that only PVP or hydrazine provides an improvement on breaking strength of pure PAN nanofiber. 7:1 PVP-PAN-$AgNO_3$ samples reduced by the arc-sol method whose light may also have a degradation effect on the polymer.

Table 4.6 : Effect of PVP on mechanical behavior of 10 % silver nitrate loaded nanofibers reduced by different reduction methods.

Samples	Tensile Strength (N/mm^2)	CV %	Tensile Strain (%)	CV %	Modulus (N/mm^2)	CV %
PAN	1.56	14.58	17.24	13.97	12.64	13.98
PAN-1PVP	1.49	19.93	11.82	21.92	11.55	33.31
PAN-Hydrazine-1PVP	3.00	24.66	16.82	28.43	17.69	25.57
PANSNp-10-Hydrazine	1.98	25.02	19.93	6.78	10.64	27.65
PANSNp-10-Xenon-sol	1.24	29.29	17.21	23.23	12.28	31.70
PAN-7PVP	3.80	19.70	48.66	16.93	10.14	27.59
PAN-Hydrazine-7PVP	9.66	24.75	32.03	34.47	61.74	26.10
PANSNp-10-Hydrazine-1PVP	4.76	29.83	39.98	24.63	10.76	33.98
PANSNp-10-Hydrazine-7PVP	3.01	14.71	18.80	31.27	11.05	35.28
PANSNp-10-Xenon-sol-7PVP	3.06	25.54	25.61	28.43	21.18	32.12

4.3 UV-Visible Spectroscopy

UV–Vis spectroscopy was used to obtain information about the formation of metallic silver nanoparticles. The maximum absorption around 410–426 nm in the UV-Vis spectrum represents the availability of silver particles in the solution.

Chemical reduction of nanofiber by hydrazine hydroxide has provided the highest absorbance in the UV-Vis spectrum than the other reduction methods. The maximum absorbance peak was observed at 426 nm. As seen from the Figure 4.1, a shift towards the higher wavelength, i.e., broader peak relates to an increase in the size the distribution of silver nanoparticles [62].

For this experimental condition, silver nanoparticle size distribution may be slightly higher for the sample reduced by the hydrazine than the sample reduced by the Xenon-solution due to broadness of its peak.

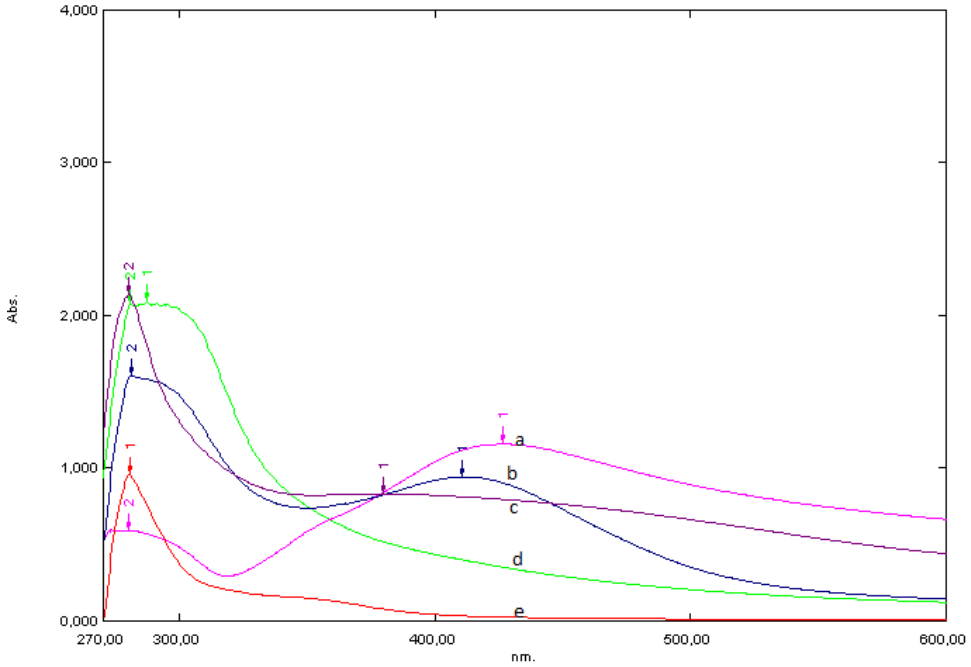

Figure 4.1 : Comparison of different reduction techniques; a- hydrazine, b- Xenon-sol, c- Xenon-web, d- Reflux methods and e- PAN/DMF solution (reference) [62].

4.4 Scanning Electron Microscopy (SEM)

Incorporation of silver nitrate into the polymer solution may cause agglomeration of silver metal nano particles and an increase in the diameter of nanofibers when the optimum ratio is exceeded. Thinner nanofiber diameters can be obtained when optimum silver nitrate ratio is used due to the increase in conductivity of jet during electrospinning as it can be seen from Table 4.7.

Table 4.7 : Effect of amount of silver nitrate and PVP loading on diameters of different nanofibers.

Samples	Diameter (nm)	CV %
PAN	312	11.3
PANSNp-1	391	17.1
PANSNp-1-Hydrazine	387	27.1
PANSNp-3-Hydrazine	358	16.0
PANSNp-10	398	29.8
PANSNp-10-Hydrazine	361	20.3
PANSNp-10-Xenon-sol	502	24.1
PANSNp-10-Hydrazine-1PVP	433	23.0
PANSNp-10-Hydrazine-7PVP	711	26.9
PANSNp-10-Xenon-sol-7PVP	1754	23.6

The presence of $AgNO_3$ (not reduced) results with an increase in diameter of nanofiber compared to the diameter of pure PAN nanofiber, however nanofibers reduced by hydrazine method have less diameters than those of samples which are not reduced possibly due to the diffusion of metallic silver atoms into inner parts of the nanofiber web forming coordination bonds with nitrile (C≡N) groups [46] and reduction of $AgNO_3$ into metallic silver nanoparticles which has not groups of NO_3 [51].

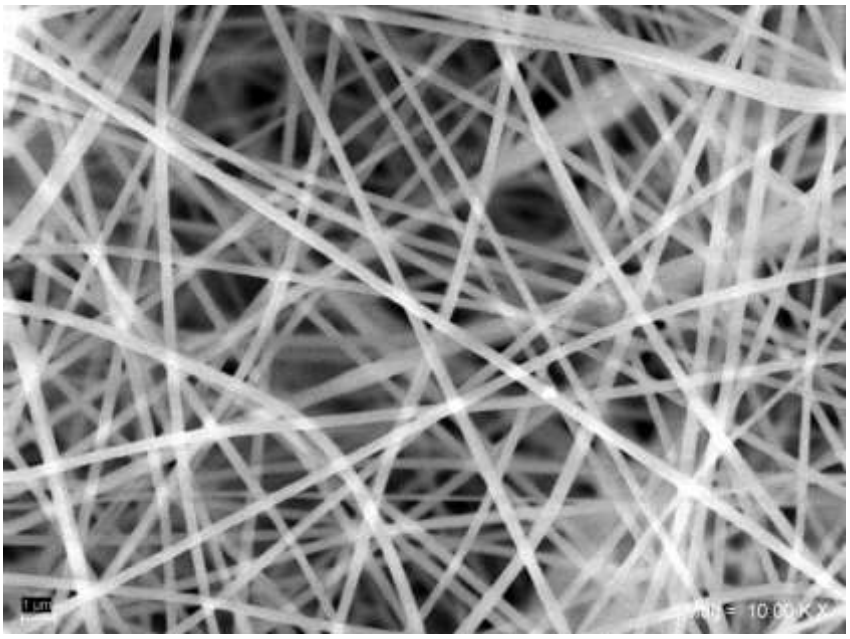

Figure 4.2 : SEM images of PAN nanofiber.

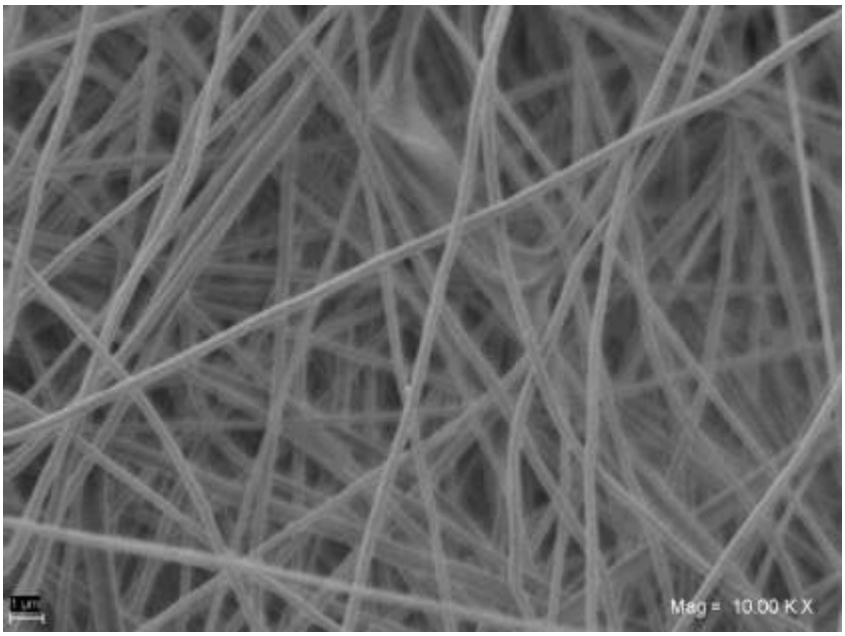

Figure 4.3 : SEM images of – PAN-hydrazine nanofiber.

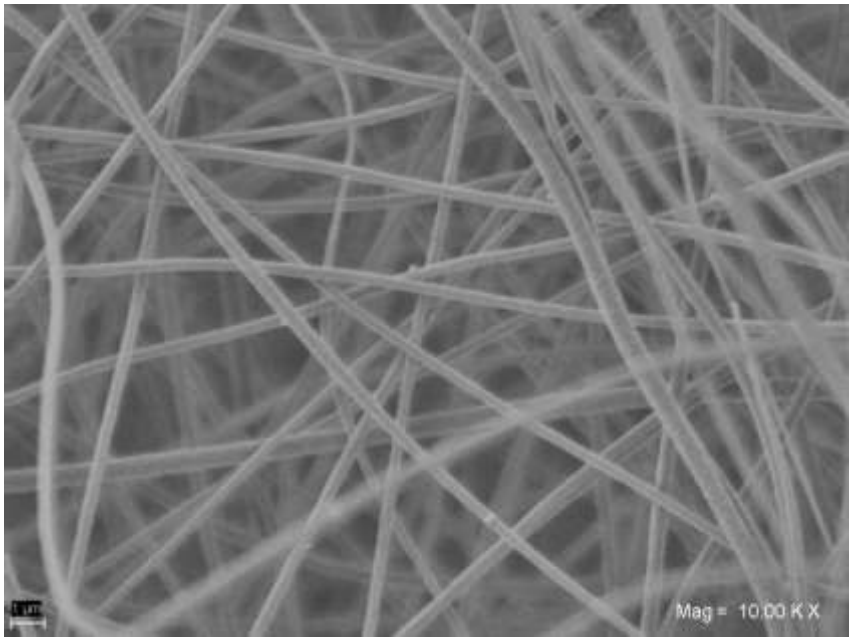

Figure 4.4 : SEM images of PAN-xenon-sol nanofiber

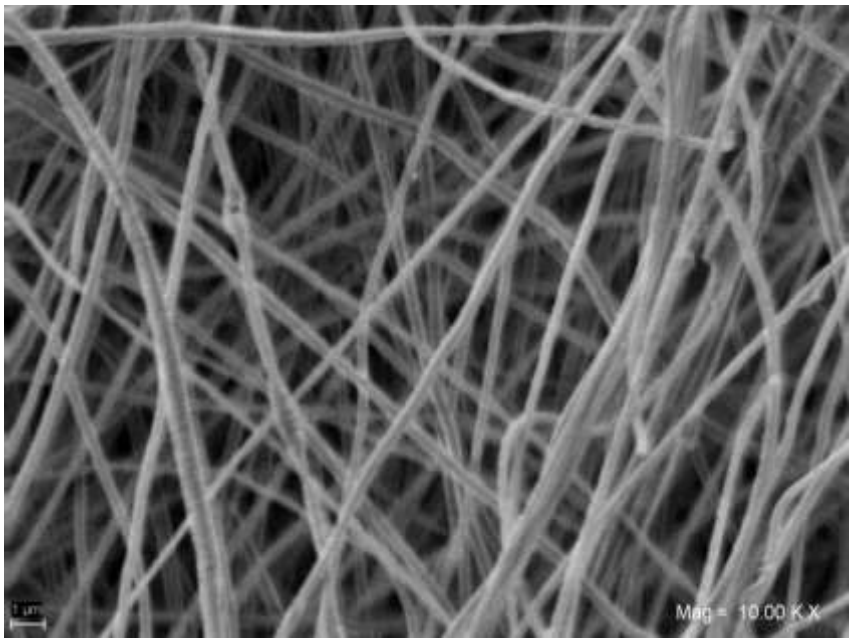

Figure 4.5 : SEM images of PANSNp-1-Hydrazine nanofiber

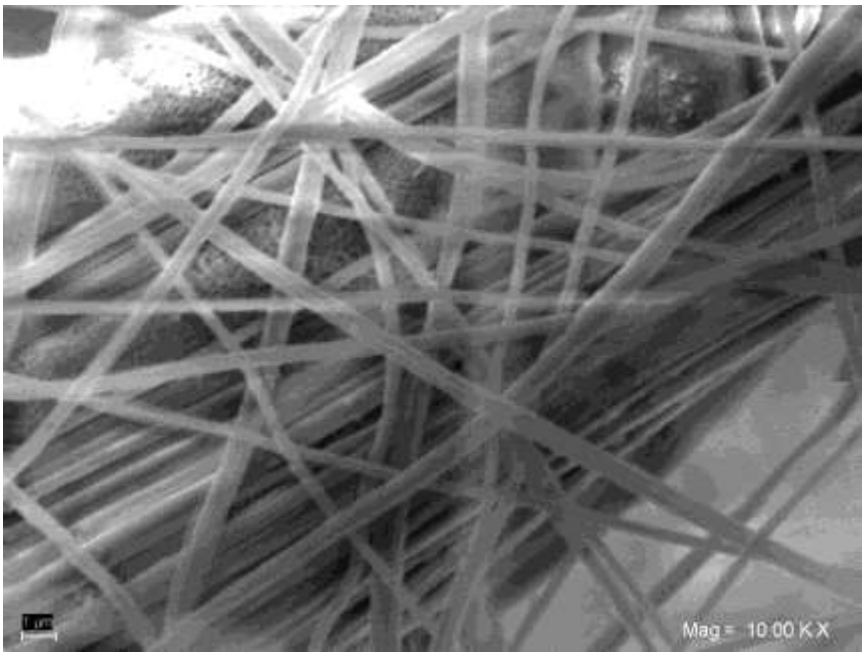

Figure 4.6 : SEM images of PANSNp-10-Xenon-sol nanofiber

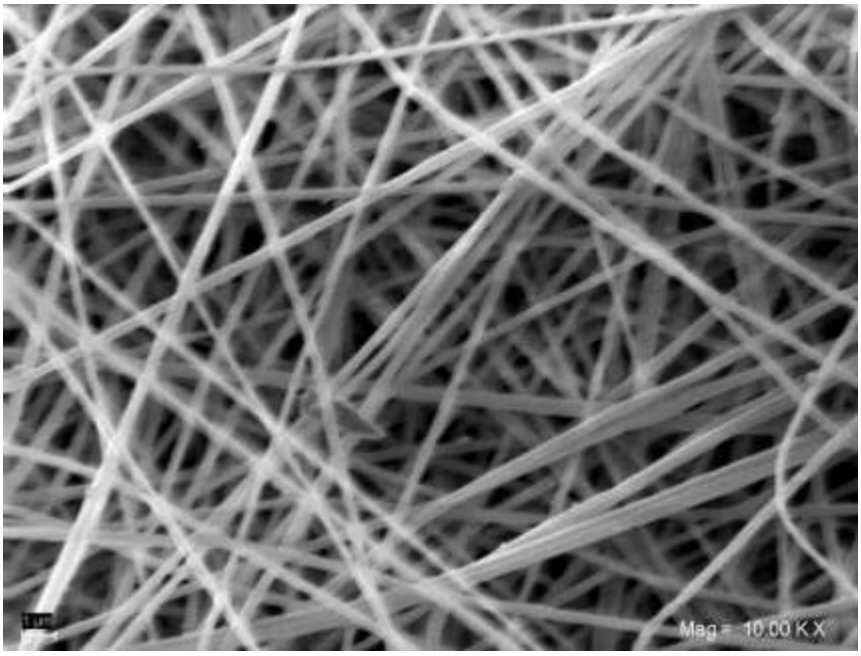

Figure 4.7 : SEM images of PANSNp-10-Hydrazine nanofiber

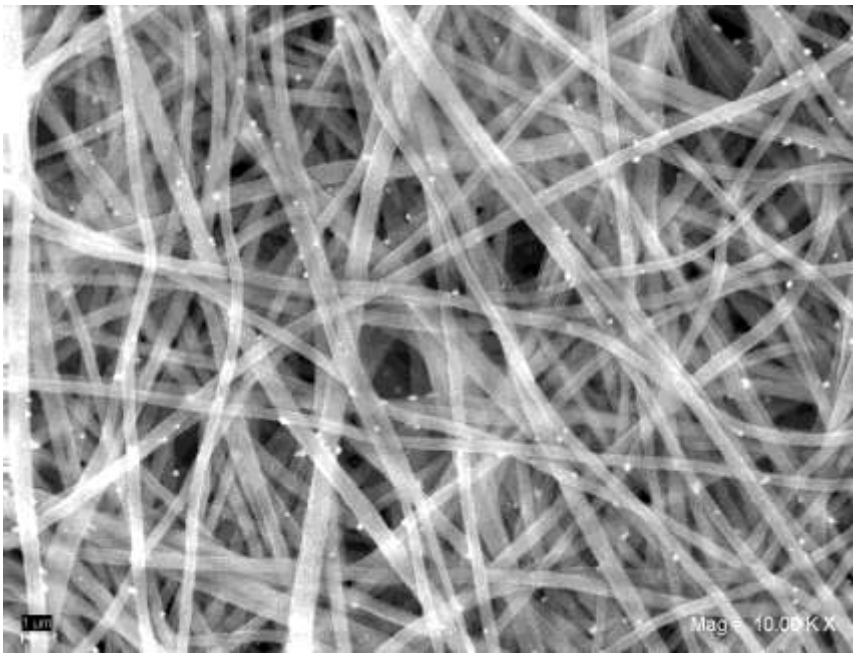

Figure 4.8 : SEM images of PANSNp-10-Hydrazine-1PVP nanofiber

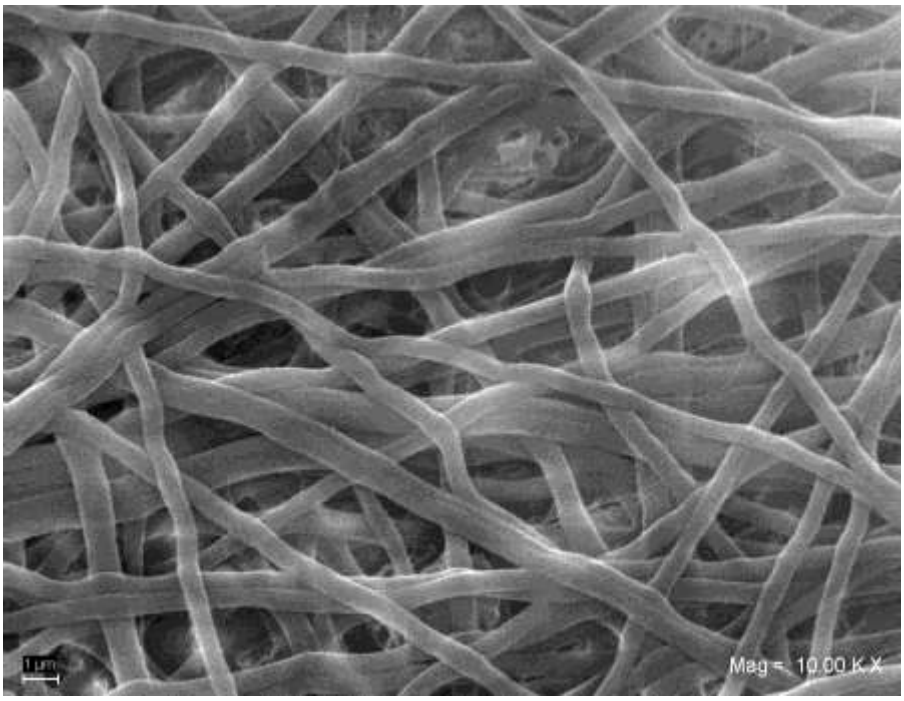

Figure 4.9 : SEM images of PANSNp-10-Hydrazine-7PVP nanofiber

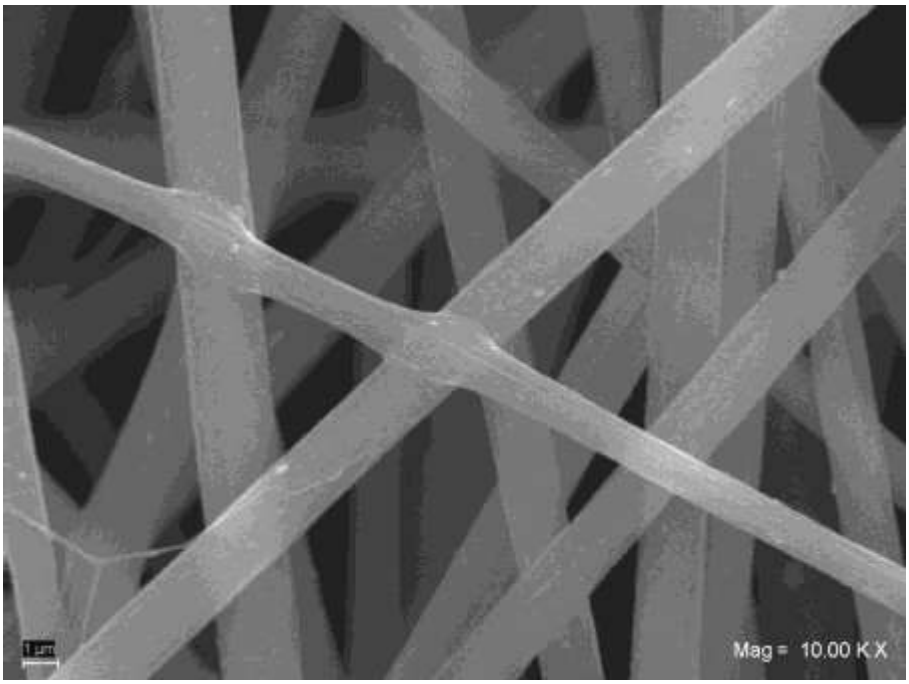

Figure 4.10 : SEM images of PANSNp-10-Xenon-sol-7PVP nanofiber

4.5 Differential Scanning Calorimetry

The thermal behavior of the composite nanofibers was examined by differential scanning calorimeter which can be seen from the Table 4.8.

Table 4.8 : Thermal properties of silver nitrate and PVP loaded nanofibers.

Samples	T_c (°C)	ΔH (J/g)
PAN	314.77	483.8
PANSNp-1	317.35	449.4
PANSNp-1-Hydrazine	318.02	466.0
PANSNp-3	323.35	491.4
PANSNp-3-Hydrazine	306.89	549.6
PANSNp-10	325.38	562.2
PANSNp-10-Hydrazine	310.29	648.2
PANSNp-10-Xenon-sol	319.47	315.8
PAN-1PVP	322.4	319.3
PAN-Hydrazine-1PVP	318.0	414.4
PAN-7PVP	327.8	161.2
PAN-Hydrazine-7PVP	310.6	446.9
PANSNp-10-Hydrazine-1PVP	317.7	304.6
PANSNp-10-Hydrazine-7PVP	322.7	474.5
PANSNp-10-Xenon-sol-7PVP	330.2	250.9

Reduction process (hydrazine method or xenon arc solution method) result with a decrease in enthalpy and an increase in cyclization temperatures (T_c) of 100% PAN nanofiber web (Figure 4.11). However, reduction process by hydrazine method results to decrease of cyclization temperature and an increase of enthalpy of composite PAN nanofiber with $AgNO_3$. An increase of $AgNO_3$ leads to an increase of enthalpy.

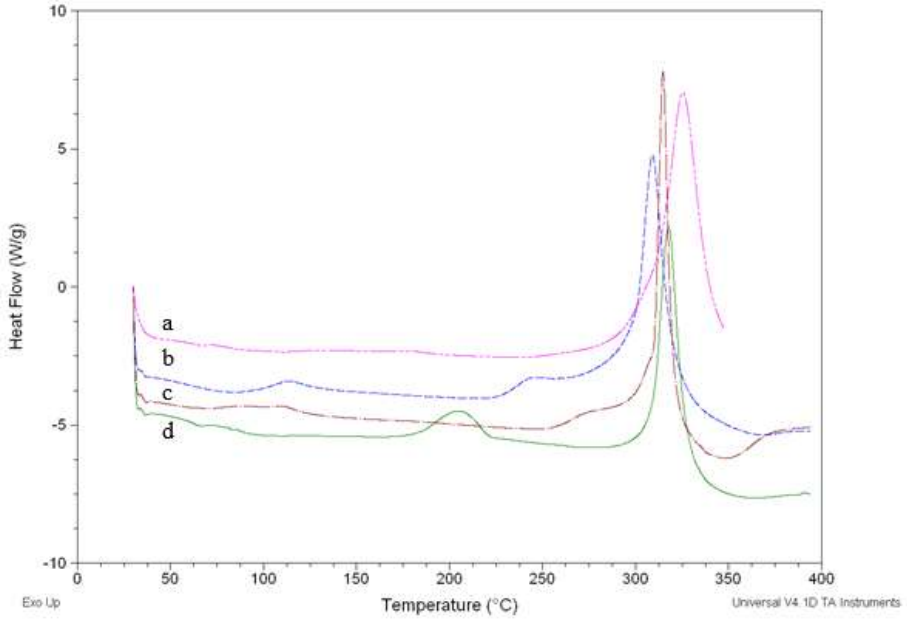

Figure 4.11 : DSC termograms of composite nanofibers: a- PANSNp-10, b- PANSNp-10-Hydrazine, c- Pure PAN, d- PANSNp-10-Xenon-sol [58].

The lowest enthalpy values was obtained from the samples reduced by xenon arc solution method; this may be due to agglomeration tendency of silver nanoparticles and degradation of polymer solution due to xenon arc light treatment.

Cyclization, dehydrogenation and oxidation reactions can be observed during the thermal processes. Nitrile (−C≡N) groups of PAN transformed into double bonded carbon-carbon (C=C) and nitrile (C=N) groups and finally leader-like molecular structure is obtained [63]. Addition of $AgNO_3$ into PAN without reduction results to an increase in both enthalpy and cyclization temperature. Thus, it can be said that application of hydrazine method and presence of silver nano particles increase the enthalpy of the composite nanofibers while arc-sol method decreases the enthalpy of the sample. This may be due to the effect of degradation by the effect of light or agglomeration of silver nano particles in the solution during the reduction process.

4.6 X-Ray Differactions (XRD)

Figure 4.12 and 4.13 represent the curve fittings of equatorial X-ray diffraction trace of electrospun nanofibers.

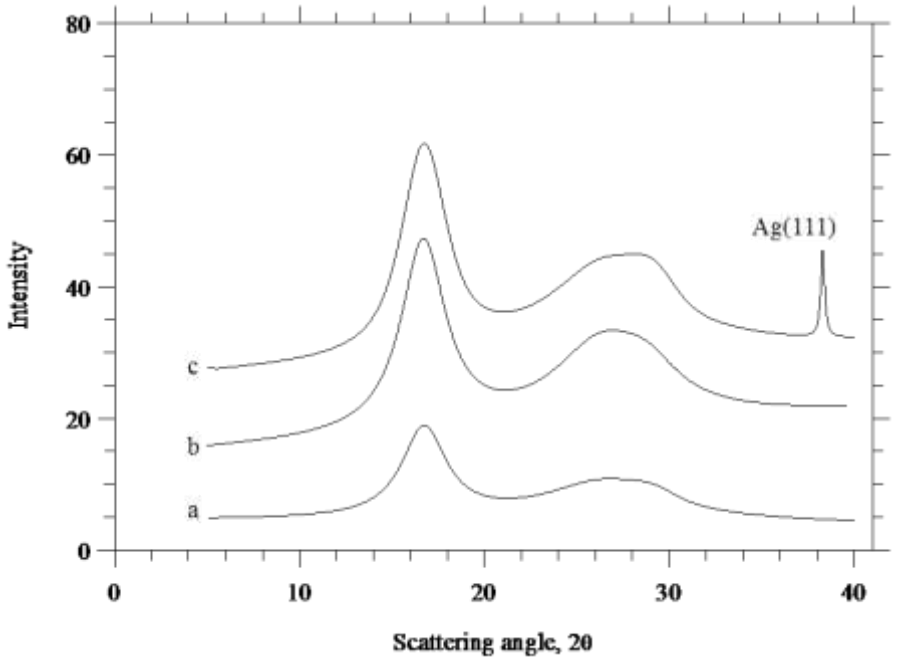

Figure 4.12 : Curve fitting of equatorial X-ray diffraction trace of electrospun nanofibers.a- Pure PAN, b- PANSNp-1, c-PANSNp-1-Hydrazine method.

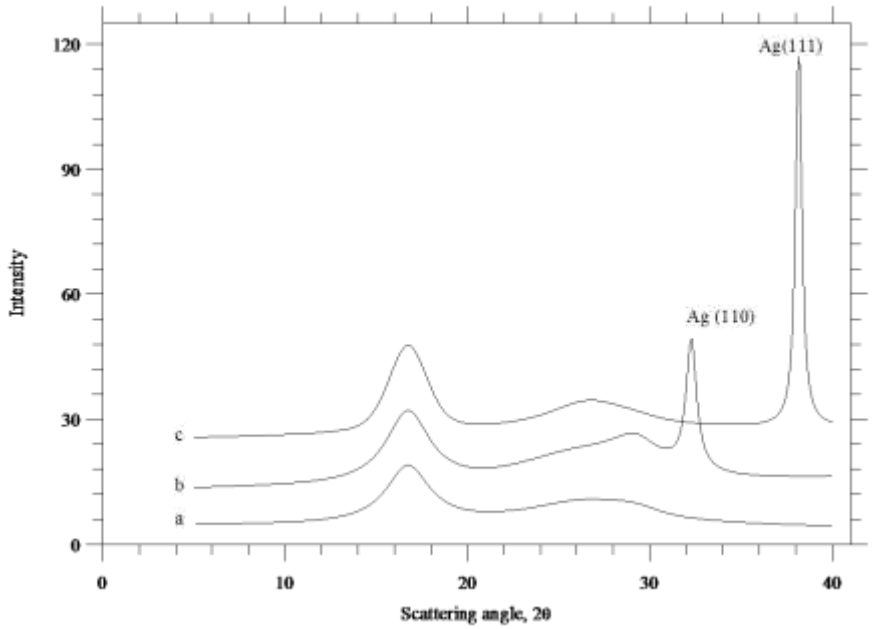

Figure 4.13 : Curve fitting of equatorial X-ray diffraction trace of electrospun nanofibers. a- Pure PAN, b- PANSNp-10, c-PANSNp-10-Hydrazine.

X-ray diffraction trace on samples containing 10 wt% $AgNO_3$ shows the presence of a very strong crystalline Ag (111) diffraction peak indicating high concentration of silver nanoparticles (Table 4.9).

Table 4.9 : Crystallinity of pure and composite PAN nanofibers from XRD

Samples	Degree of Crystallinity (%)	PAN (100) (°2θ)	PAN (110) (°2θ)	Ag (°2θ)
PAN	22.6	16.70	29.20	-
PANSNp-1	27.0	16.70	29.20	-
PANSNp-1-Hydrazine	21.0	16.70	29.20	38.2 (111)
PANSNp-10	14.2	16.70	29.20	31.0 (110)
PANSNp-10-Hydrazine	17.6	16.70	29.20	38.2 (111)

The presence of high concentration of silver nanoparticles (10 wt% $AgNO_3$) decreases the crystallinity of PAN nanofiber (100% PAN). The agglomeration of the silver nitrate may cause an obstacle for the formation of the some crystalline structure in the PAN chains [51]. Thus, the presence of high concentrations of Ag^+ ions and reduced silver (Ag^o) nanoparticles in the structure disturbs the crystalline structure causing the reduction of the degree of crystallinity [64].

4.7 Antibacterial Efficiency Test

It can be seen that 99. 99 % efficiency was obtained from three different reduction methods after 24 h from the Table 4.10.

Table 4.10 : Antimicrobial efficiency for nanofibers reduced by different reduction methods

Samples	AntimicrobialEfficiency (%)
PANSNp-1- Hydrazine	45.000
PANSNp-3- Hydrazine	99.999
PANSNp-10- Xenon-sol	99.999
ANSNp-10- Xenon-web	99.996
PANSNp-10- Hydrazine	99.988

Although the reduction by the hydrazine method provided higher peak in the UV-Vis spectra than the other methods it has been seen that the amount of reduced silver ions in all three methods were enough to obtain 99% antimicrobial efficiency when 10%

$AgNO_3$ was used [62]. Also it can be conculuded that 1 % of silver nitrate loading was not sufficient for the obtaining antimicrobial efficiency. Figure 4.14 represents the antimicrobial efficiency test.

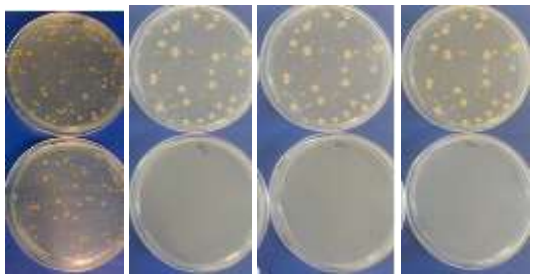

Figure 4.14 : Antimicrobial efficiency test for nanowebs; a-pure PAN, b- PANSNp-10-Hydrazine, c- PANSNp-10-Xenon-web, d- PANSNp-10-Xenon-sol method [62].

4.8 Yellowness

It can be seen from the figure that reduction of silver nano particles cause yellowness on the color of nanofibers. The yellow-brown color can be assumed as an indicator for the reduction of silver nano particles. The most yellowness is seen from the reduction by hydrazine method which is implying the most effective reduction method is hydrazine. Also this result can be supported by UV-Vis. spectra (Figure 4.1)

Figure 4.15 : Yellowness comparison of the nanofibersreduced with different techniques; a- PANSNp-10, b- PANSNp-10- Xenon-sol, c-PANSNp-10- Xenon-web, d- PANSNp-10- Hydrazine methods.

5. CONCLUSIONS AND RECOMMENDATIONS

From these studies following conclusions were obtained:

Reduction by hydrazine hydroxide solution or Xenon arc light resulted with a slight decrease in the diameter of pure PAN nanofiber. The presence of $AgNO_3$ (unreduced) resulted with an increase in diameter of nanofibers compared to the diameter of pure PAN nanofiber due to an addition of new material into polymer matrix or agglomeration of nanofiller. Nanofibers containing reduced silver nanoparticles were found to have less diameters than those of the samples which contained unreduced silver.

Nanofibers reduced by xenon arc solution method were found to have the highest diameter. This may be a direct result of agglomerated silver nanoparticles in the solution before electrospinning.

The optimum silver nitrate ratio is found that 3 wt %. As agglomeration of silver nanoparticles caused a decrease in the electrical conductivity, 10 wt% silver nitrate loaded PAN was found to have lower electrical conductivity values than that of 3 wt%. Highest electrical conductivity values was obtained from 3 wt% silver nitrate loaded PAN nanofiber.

Composite nanofiber reduced by Xenon arc solution method had less strength than that of reduced by hydrazine method due to both agglomeration tendency and degradation of polymer.

It has been seen that the reduced amount of silver ions in all three methods Xenon-sol, Xenon-web and hydrazine method were enough to provide 99% antimicrobial efficiency when 10% $AgNO_3$ was used. 1% of silver nitrate loading was not provide an antimicrobial efficiency.

PVP loading into the polymer solutions causes an increase in the diameters of nanofibers. High amount of PVP usage does not provide desired stabilization of silver nano particles and may cause agglomerations.

Optimum ratio for obtaining the best results from PVP is 1:1 loading. This ratio provides better mechanical properties.

Reduction with hydrazine hydroxide required more cyclization energy and less cyclization temperature.

REFERENCES

[1] **Eddie, D. D.** (2003). *The Effect Of Processing On The Structure And Properties*, Chapter 2, Taylor & Francis.

[2] **Nataraj, S. K., Yang, K. S., Aminabhavi, T. M. (**2011). Polyacrylonitrile-based nanofibers—A state-of-the-art review, *Progress in Polymer Science 37*, 487– 513.

[3] **Khajuria, A., Balaguru, P. N.** (1992). *Plastic shrinkage characteristics of fiber reinforced cement composites*. In: Swamy RN, editor. Fibrereinforced cement composites. London: Routledge, Taylor & Francis; 1992. 82–90.

[4] **Bai, Y. J., Wang, C. G., Lun, N., Wang, Y. X., Yu, M. J., Zhu, B.** (2006). HRTEM microstructures of PAN precursor fibers. *Carbon, 44*, 1773–8.

[5] **Mittal, J., Mathur, R. B., Bahl, O. P. (**1997). Post spinning modification of PAN fibers – a review. *Carbon 35*, 1713–22.

[6] **Xiaomei, Z., Juan, H., Jiongxin, Z., Youwei. Z,, Ding, P.** (2007). Investigating the jet stretch in the wet spinning of PAN fiber. *J Appl Polym Sci , 106,* 2267–73.

[7] **Toshiyuki, K., Seiji, T.,** High strength polyacrylonitrile fiber and method of producing the same. US Patent 4535027; 1985.

[8] **Ijima S.** (1991). Helical microtubules of graphitic carbon. *Nature, 354*, 53–8.

[9] **Ren, Z. F., Huang, Z. P., Xu, J. H., Bush, P., Siegal, M. P., Provencio, P. N**. (1998). Synthesis of large arrays of well-aligned carbon nanotubes on glass. *Science, 282,* 1105–7.

[10] **Formhals, A. (**1934). Process and apparatus for preparing artificial threads. US Patent 1975504; 1934.

[11] **Baumgarten, P. K.** (1971). Electrostatic spinning of acrylic microfibers. *J Colloid Interface Sci, 36*, 71–9.

[12] **Larronda, L., St John Manley, R.,** (1981). Electrostatic fiber spinning from polymer melts. I. Experimental observations on fiber formation and properties. *J Polym Sci Polym Phys Ed,19*, 909–20.

[13] **Farah, E. A., Boor, S. L., Hashaikeh, R. (**in press). A review on electrospinning for membrane fabrication: Challenges and applications, *Desalination, 356*, 15–30.

[14] **Xing, X., Wang, Y., Li, B.** (2008). Nanofibers drawing and nanodevices assembly in poly(trimethylene terephthalate).

[15] **Feng, L., Li, S.H., Zhai, J., Song, Y. L., Jiang, L., Zhu, D. B.** (2003). Template based synthesis of aligned polyacrylonitrile nanofibers using a novel extrusion method, *Synth. Met. 135–136*, 817–818.

[16] **Ma, P. X., Zhang, R. (**1999). Synthetic nano-scale fibrous extracellular matrix, *J. Biomed. Mater. Res. 46*, 60–72.

[17] **Ramakrishna, S.** (2005). An Introduction to Electrospinning and Nanofibers, *World Scientific*.
[18] **Frenot, A., Chronakis, I. S.** (2003). Polymer nanofibers assembled by electrospinning, *Curr. Opin. Colloid Interface Sci. 8*, 64–75.
[19] **Li, Z., Wang, C.** (2013). Effects of working parameters on electrospinning, One-Dimensional Nanostructures, *Springer Berlin Heidelberg*, 15–28.
[20] **Wendorff, J. H., Agarwal, S., Greiner, A.** (2012). Electrospinning: Materials, Processing, and Applications, Wiley, 2012.
[21] **Stranger, J., Tucker, N., Staiger**, **M.** (2009). Electrospinning, *Smithers Rapra, Shrewsbury, Shropshire, GBR.*
[22] **Martins, A., Reis, R. L. and Neves, N. M.** (2008). Electrospinning: processing technique for tissue engineering scaffolding, *Int Mater Rev*, 53, 257–74.
[23] **Doshi, J. and Reneker, D. H.** (1995). Electrospinning process and applications of electrospun fibers, *J Electrostat*, 35, 151–60.
[24] **Fong, H., Chun, I. and Reneker, D. H.** (1999). Beaded nanofibers formed during electrospinning, *Polymer*, *40*, 4585–92.
[25] **Demir, M. M., Yilgor, I., Yilgor, E. and Erman, B.** (2002). Electrospinning of polyurethane fibers, *Polymer*, *43*, 3303–9.
[26] **Theron, S. A., Zussman, E. and Yarin, A. L.** (2004). Experimental investigation of the governing parameters in the electrospinning of polymer solutions, *Polymer*, 45, 2017–30.
[27] **Jin, H. J., Chen, J. S., Karageorgiou, V., Altman, G. H. and Kaplan, D. L.** (2004). Human bone marrow stromal cell responses on electrospun silk fibroin mats, *Biomaterials*, *25*, 1039–47.
[28] **Casper, C. L., Stephens, J. S., Tassi, N. G., Chase, D. B. and Rabolt, J. F.** (2004). Controlling surface morphology of electrospun polystyrene fibers: Effect of humidity and molecular weight in the electrospinning process, *Macromolecules*, 37, 573–8.
[29] **Ding, B., Kimura, E., Sato, T., Fujita, S. and Shiratori, S.** (2004). Fabrication of blend biodegradable nanofibrous nonwoven mats via multi-jet electrospinning, *Polymer*, 45, 1895–902.
[30] **Kim, G. H.** (2006). Electrospinning process using field-controllable electrodes. *J Polym Sci, Part B: Polym Phys*, 44, 1426–33.
[31] **Katta, P., Alessandro, M., Ramsier, R. D. and Chase, G. G**. (2004). Continuous electrospinning of aligned polymer nanofibers onto a wire drum collector. *Nano Lett*, 4, 2215–18.
[32] **Ahn, Y. C., Park, S. K., Kim, G. T., Hwang, Y. J., Lee, C. G., Shin, H. S. and Lee, J. K.** (2006). Development of high efficiency nanofilters made of nanofibers, *Curr Appl Phys*, *6*, 1030–5.
[33] **Gibson, P., Schreuder-Gibson, H. and Rivin, D.** (2001). Transport properties of porous membranes based on electrospun nanofibers. *Colloid Surface A*, 187, 469–81.
[34] **Barrasa, J. G., López-de-Luzuriaga, J. M., Monge, M**. (2011). *Cent. Eur. J. Chem, 9(1)*, 7-19.
[35] **Klasen, H. J**. (2000*). Burns 26*, 117.
[36] **Barber, D.J., Freestone, I. C.** (1990). *Archaeometry*, 32, 33.
[37] **Pérez-Arantegui, j.,Larrea**, **A.**, 2003, Trends Anal. Chem. Pp. 22, 327.
[38] **Burda, C., Chen, X., Narayanan, R., El-Sayed**, **M. A.** (2005). *Chem. Rev. 105*, 1025.

[39] **Lee, P. C., Meisel, D. J. (**1982). *Phys. Chem*. 86, 3391.
[40] **Creighton, J. A., Blatchford, C. G., Albrecht, M. G**. (1979). *J. Chem. Soc. Farad. Trans. II 75*, 790.
[41] **Kudryashov, M.A., Mashin, A.I., Tyurin, A.S., Fedosov, A.E., Chidichimo, G., De Filpo G.** (2011). Morphology of a Silver/Polyacrylonitrile Nanocomposite, *Technical Physics, 2011, Vol. 56, No. 1*, 92–96.
[42] **Mahapatra, A., Garg, N., Nayak, B. P., Mishra, B. G., Hota, G.** (2012). Studies on the synthesis of electrospun PAN–Ag composite nanofibers for antibacterial application. *J Appl Polym Sci 500 124*, 1178–1185.
[43] **Shi, Q., Vitchuli, N., Nowak, J., Caldwell, J. M., Breidt, F., Bourham, M., Zhang, X., McCord, M.** (2011). Durable antibacterial Ag/ polyacrylonitrile (Ag/PAN) hybrid nanofibers prepared by atmospheric plasma treatment and electrospinning. **Eur Polym J 47**, 1402–1409.
[44] **Rujitanaroj, P., Pimpha, N., Supaphol, P.** (2010). Preparation, characterization, and antibacterial properties of electrospun polyacrylonitrile fibrous membranes containing silver nanoparticles, *J Appl Polym Sci 116,* 1967–1976.
[45] **Sichani, G. N., Morshed, M., Amirnasr, M., Abedi, D. (**2010). In situ preparation, electrospinning, and characterization of polyacrylonitrile nanofibers containing silver nanoparticles. *J Appl Polym Sci 116,* 1021–1029.
[46] **Wang, Y., Yang, Q., Shan, G., Wang, C., Du, J., Wang, S., Li, Y., Chen, X., Jing, X., Wei, Y.** (2005). Preparation of silver nanoparticles dispersed in polyacrylonitrile nanofiber film spun by electrospinning. *Mater Lett 59*, 3046–3049.
[47] **Lee, H. K., Jeong, E. H., Baek, C. K., Youk, J. H.** (2005) One-step preparation of ultrafine poly(acrylonitrile) fibers containing silver nanoparticles. *Mater Lett 59*, 2977–2980.
[48] **Ijeri, V.S., Nair, J. R., Gerbaldi, C., Genolli, R. S., Bordoardo, S., Bongiovanni, R. M. (**2010). An elegant and facile single-step UV-curing approach to surface nano-silvering of polymer composites, *Soft Mater, 6*, 4666–4668.
[49] **Tyurin, A., Filpo, G. D., Cupelli, D., Nicoletta, F. P., Mashin, A., Chidichimo, G.** (2010) Particle size tuning in silver-polyacrylonitrile nanocomposites. *Express Polym Lett 4(2),* 71–78.
[50] **Lee, D. Y., Lee, H. K., Kim, B.Y., Cho, N. I**. (2010). *J Sol-Gel Sci Technol, 54*, 63–68.
[51] **Demirsoy, N., Ucar, N., Onen, A., Karacan, I., Kızıldag, N., Eren, O., Borazan, I. (**2014) The effect of dispersion technique, silver particle loading, and reduction method on the properties of polyacrylonitrile–silver composite nanofiber, *Journal of Industrial Textile*, 15.
[52] **Bai, J., Yan, Q., Wang, S., Li, Y.** (2011) Preparation and characterization of electrospun Ag/polyacrylonitrile composite nanofibers. *Korean J Chem Eng 28(8)*, 1761–1763.
[53**] Wall, M. J. and Frank, G. J**. A study of the spectral distributions of sun-sky and xenon-arc radiation in relation to the degradation of some textile yarns: Part I: Yarn degradation. *Text Res J 1971; 41*, 32–38.
[54] **Reichmanis, E., Frank, C. W., O'Donnell, J. H., Hill, D. J. T.** (1993). Radiation effects on polymeric materials, a brief overview. Irradiation of

polymeric materials. American Chemical Society, ACS Symposium Series, Washington, DC, pp 1–8.

[55] **Folttmann, H., Quadir, A., (**2008). Polyvinylpyrrolidone (PVP) – One of the Most Widely Used Excipients in Pharmaceuticals: An Overview, *Drug Delivery Technology, Vol 8 No 6.*

[56] **Malina, D., Sobczak-Kupıec, A., Wzorek, Z., Kowalski, Z.** (2012). Silver nanoparticles synthesis with different concentrations of polyvinylpyrrolidone. *Dig J Nanomater Biostructures, 7(4),* 1527–1534.

[57] **Jin, W.J., Lee, H. K., Jeong, E. H., Park, W. H., Youk, J. H.** (2005). Preparation of polymer nanofibers containing silver nanoparticles by using poly(N-vinylpyrrolidone). *Macromol Rapid Commun 26*, 1903–1907 .

[58] **Ucar, N., Demirsoy, N., Onen, A., Karacan, I., Kızıldag, N., Eren, O., Vurur, O. F., Sezer, E., Ustamehmetoğlu, B. (**2014). The effect of reduction methods and stabilizer (PVP) on the properties of polyacrylonitrile (PAN) composite nanofibers in the presence of nanosilver. *J Mater Sci, DOI 10.1007/s10853-014-8748-4*.

[59] **ASTM D257-7** (2013) Standard test methods for DC resistance or conductance of insulating materials

[60] **ASTM D4496-13** (2013) Standard test method for D-C resistance or conductance of moderately conductive materials.

[61] **Abdo, H., S., Khalil, K., A., Al-Deyab, S. S., Altaleb, H., Sherif, E. S. M.** (2013). Antibacterial effect of carbon nanofibers containing Ag nanoparticles. *Fiber Polym 14(12),* 1985–1992.

[62] **Demirsoy, N., Ucar, N., Onen, A., Karacan, I., Kızıldag, N., Eren, O., Vurur, O. F., Sezer, E., Ustamehmetoglu, B. (**2014). The Importance Of Reduction Methods And Ratio Of Pvp For Composite Pan-Silver Nanofiber. *International Congress, AUTEX*, May 26-28, 2014 Bursa, Turkey.

[63] **Almuhamed, S., Khenoussi N., Schacher, L., Adolphe, D., Balard, H.** (2012) Measuring of electrical properties of MWNT-reinforced PAN nanocomposites. *J Nanomater. doi:10.1155/2012/ 750698.*

[64] **Chen Y, Liu H and Zhang Z**. (2010). Characterization and morphology of composites prepared from polyacrylonitrile and silver nitrate. *Appl Mech Mater, 26–28,*159–162.

CURRICULUM VITAE

Name Surname: Nesrin DEMİRSOY

Place and Date of Birth: 23.03.1988

E-Mail: nesrindemirsoy@gmail.com

B.Sc.: Marmara University

PUBLICATIONS, PRESENTATIONS AND PATENTS ON THE THESIS:

- Demirsoy, N., Ucar, N., Onen, A., Karacan, I., Kızıldag, N., Eren, O., Vurur, O. F., Sezer, E., Ustamehmetoglu, B.**,** 2014. The Importance Of Reduction Methods And Ratio Of Pvp For Composite Pan-Silver Nanofiber. *International Congress, AUTEX*, May 26-28, 2014 Bursa, Turkey.

- Demirsoy, N., Ucar, N., Onen, A., Kızıldag, N., Vurur, O. F., Eren, O., Karacan, I., 2014. Investigation of Electrical, Thermal and Structural Properties on Polyacrylonitrile Nano-Fiber, *International Congress, WASET*, August 14-15, 2014 Venice, Italy.

- Demirsoy, N., Ucar, N., Onen, A., Karacan, I., Kızıldag, N., Eren, O., Borazan, I., 2014. The effect of dispersion technique, silver particle loading, and reduction method on the properties of polyacrylonitrile–silver composite nanofiber, *Journal of Industrial Textile*, DOI:10.1177/1528083714553690.

- Ucar, N., Demirsoy, N., Onen, A., Karacan, I., Kızıldag, N., Eren, O., Vurur, O. F., Sezer, E., Ustamehmetoğlu, B., 2014. The effect of reduction methods and stabilizer (PVP) on the properties of polyacrylonitrile (PAN) composite nanofibers in the presence of nanosilver. *J Mater Sci*, DOI: 10.1007/s10853-014-8748-4.